TRANSITION METAL ION CATALYSED OXIDATION OF SOME ORGANIC COMPOUNDS

THESIS

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By

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Dedicated

To

My

Husband

Mr. Ashish Kumar Gupta

TO MY REVERED GUIDE

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CHAPTER-I

INTRODUCTION

In chemistry, we deal with different kinds of matter, their interaction and changes. The speed of chemical changes vary from micro seconds to years. The aim of chemistry is not only to determine the composition of substance and such changes which they undergo but, also to plan and control these changes and create new compounds to offer mankind to better and fuller tomorrow.

Most prominent chemist has great interest in kinetical investigation due to its significant role in the academic field of research and development. These studies have wide application in chemical engineering and industries.

Chemical kinetics is the systematic detailed study of the rate of chemical reactions and the factors which control and influence their progress and course. The ultimate object is to ascertain the behaviour of molecules and ions during the course of a chemical reaction and to draw definite conclusion about their detailed mechanism i.e. the specific course which it follows. Chemical kinetics might very well be called as chemical dynamics.

Kinetics is concerned fundamentally with the details of the process whereby a system gets from one state to another and with the time required for the transition. Several theories based on kinetic theory and statistical mechanics have been developed to account for such chemical changes. Equilibrium can also be treated in principle on the basis of kinetics as that situation in which the rate of the forward and reverse reactions are equal. The converse is not true, a reaction rate cannot be understood on the basis of thermodynamics alone. Therefore, chemical kinetics may be considered a more powerful tool in the hands of chemist to elucidate the reaction mechanism.[1]

Historically, modern kinetics can be dated from the first publication in 1864, of the formulation of the law of mass action by Gulberg & Waage, [2] which express in its eventual refinement, the rate of a chemical reaction in terms of the concentration of the participating reactants in a manner related to the microscopic pathway by which the changes occur.

There are many common concepts in the kinetics of both gaseous and liquid phase reaction, viz; the reaction rates in both cases are related to the rates of encounters between the reactants and are expressed by similar mathematical expressions. However, the kinetic studies of gaseous reactions have been found to be much simpler as compared with the reactions in solutions which are much more complex and present many complications such as the uncertainty of reacting species, their activities and the solution of different species. In spite of these difficulties most of reactions have been studied in solution phase. There are several factors which provide considerable information about the mechanism of reaction in solution. The most important being the order of reaction with respect to different reactants, the effect of catalyst, ionic strength, [3] solvent[4] and dielectric constant[5] of the medium and temperature. The identification of intermediate species and information about their structure and use of 'isotopic method' have also proved to be of great help in establishing the reaction mechanism.

Kinetics is thus the study of rate of chemical reactions and molecular processes by which the reaction occur[6] and is fundamentally concerned with the details whereby a system gets from one state to another with time required for the transition. Kinetic studies along with stoichiometry studies provide the most powerful methods of determining reaction mechanism. The

main use of rate data in elucidating the reaction mechanism is in the establishment of kinetics and stoichiometry.

The chemical stoichiometry is the sum of two or more terms. One of which is slow and is said to be rate determining step.[7] Thus rate measurements themselves are in combination with knowledge of appropriate thermodynamical properties of the system may be sufficient for understanding of reaction mechanism. Therefore, chemical kinetics may be considered a powerful tool in the hands of chemist to elucidate reaction mechanism.[8]

Reactions involving the catalytic oxidation of the organic compounds are the most interesting and useful of the chemical processes. A large number of workers have their interest in the field of oxidation–reduction process.[9-12] The catalytic reactions can be studied under two different heading; heterogeneous reactions and homogenous reactions. I shall restrict myself here to the subject of homogeneous catalysis; this is partly because a study of homogeneous catalysis is of more general importance in understanding the mechanism of chemical reactions and partly because heterogeneous catalysis is an extensive, largely self-contained subject in itself. Consequently, its discussion would lead us too for a field.[13]

An interesting example of the homogeneous catalysis is the oxidation of organic compounds by Ce(IV) catalysed by chromium(III) salts.[14,15] The proposed mechanism shows a rapid reaction between chromium(III) and cerium(IV) followed by a rate determining reaction between the organic substrate and the chromium, which is in a valence state greater than three most likely it is chromium(VI). This system examplifies the fact that oxidation potential can not only be used as a guide for the oxidation of

compounds since cerium (IV)-(III) has a higher oxidation-reduction potential than chromium(VI). Similarly Mn(II) is also employed in the same system as catalyst in oxidation of some compounds[16] by cerium(IV) in acidic medium and also in the same system (Ag^+) is used as catalyst.[17]

Some work has been done using transition metal ions as catalyst in homogeneous medium. A very interesting and effective catalyst for the oxidation of organic compounds in solution is osmium tetraoxide. The catalytic actions of this reagent are well known with several couples. It has frequently been used as a catalyst for the hydroxylation of ethylenic doubles bonds. Criegee[18,19] in a classic piece of work that the reaction involved an osmium(VI) intermediate which can in many cases be isolated. Zelikoff and Taytor[20] has studied the oxidation of fumaric and maleic acids by employing potassium chlorate using osmium tetraoxide as catalyst in acid medium. They showed that slow addition of osmium tetraoxide to double bond occurs forming osmic ester followed by fast oxidation with chlorate yielding tartaric acid and osmium tetraoxide.

But it was further observed that the quantitative regeneration of the catalyst by chlorate was not a very fast process. The reagent was further employed for the catalytic oxidation of benzene in tert. butanol with hydrogen peroxide[21] as the regenerating source. But the details of the kinetic investigation were still lacking. Very recently in our laboratory the oxidation of few unsaturated compounds like acrylic acid, methacrylic acid and crotonic acid has been studied by cerium(IV) employing Os(VIII) as homogeneous catalyst.[22]

Copper(II)-(I) couple was employed for the oxidation of ethylene to acetaldehyde in presence of palladium chloride used as the homogeneous

See reference on Pg. No.11

catalyst.[23] The kinetics of the palladium(II) catalysed oxidation of acrylic, methacrylic and crotonic acid by vanadium(V) in acidic medium at constant ionic strength exhibit zeroth order dependence on vanadium(V) and first order dependence on Pd(II) and the unsaturated acid.[24,25] Direct addition of hydrogen peroxide to compounds to produce glycols, catalysed by various inorganic salts, has been described very well by Mugdan and Young.[26] These reactions were used for the synthetic work with no adequate attempt made to study the kinetics and the mechanism of the reactions which occur. A successful kinetic study was made by Martell and Khan[27] a metal ion and metal chelate catalysed oxidation of ascorbic acid by molecular oxygen. In all such oxidations, a suitable catalyst regenerating oxidant is needed.

Among the most important common oxidants which have received considerable emphasis leading to mechanistic studies are permanganate, chromic acid, Ce(IV), Co(III), Mn(III), V(V), lead tetra acetate, ozone and hydrogen peroxide etc. However, these oxidants have been mainly used in acidic medium. On the other hand the oxidants used in the, alkaline medium are ammonical silver nitrate, Fehling's solution, permanganate and ferricyanide. Out of these oxidants ferricyanide is more convenient to be used due to many reasons. The greatest advantage is that the reaction mixture remains homogeneous while in the case of ammonical silver nitrate, Fehling's solution, the reaction mixture becomes heterogeneous and hence the results are not reproduceable in these cases. Ferricyanide is essentially a substitution inert transition metal complex,[28] it does not exchange its ligands at a rate fast enough to complete with rapid electron transfer i.e.; oxidation-reduction reactions. Therefore, oxidations by ferricyanide occur by means of non-bonded or outer sphere process where by an electron is transferred from the substrate to the metal ion through the cyano-ligand.

Moreover, the potential of ferricyanide-ferricyanide couple does not alter significantly over a wide range of hydroxide ion concentrations. The variation of potential has been observed only of the order of 0.05v in the concentration range of sodium hydroxide between 1.0N to 5.0N, whereas the redox potential of most of the other systems becomes considerably negative in the alkaline medium.[29] Therefore, in the present work, the ferro-ferricyanide couple has been employed as an oxidant to study the homogeneously catalysed reactions of some organic compounds.

Hexacyanoferrate(III) oxidations have recently received much attention due to its cheap availability and less complexity involved in the estimation. Reviews presenting very interesting information have also been written by many authors.[30-33] Very often, it has been suggested that Hexacyanoferrate(III) functions in oxidation-reduction reactions as a simple one electron abstracting reagent based on the assumption that the slight interaction of the electronic levels of oxidant and preductant is sufficient to permit electron transfer.

$$Fe(CN)_6^{-3} + e^{-1} \longrightarrow Fe(CN)_6^{-4}$$

The preliminary work of Conant and Coworkers[34] on the oxidation by Hexacyanoferrate(III) and the work of Waters and Speakmann[35] clearly indicates that in the oxidation of organic compounds, the charge transfer process is not possible.

The kinetics of Hexacyanoferrate(III),[36-38] oxidations of a number of organic substrates are known in alkaline medium and are affected very little by the change of pH. Conant and Coworkers[34] were of the view that in the alkaline Hexacyanoferrate(III) oxidation of aldehyde, ketones and

See reference on Pg. No.12

nitroparaffins, not two but a single step was rate determining and the oxidation process involved no free radial formation. On the other hand, in the oxidation of phenols etc., coloured and stable radicals were detected.[39] The exchange of cyanide ligand was given by Kolthoff and Coworkers[40,41] in the oxidation of phenols.

The oxidation of thiols was also re-examined by Wiberg and Coworkers[42] with the help of isotopic exchange. These workers observed that there was exchange of cyanide ligand and the oxidations invariably occurred via a direct charge transfer process. From these studies it is now quite obvious that the oxidation occurred mainly via direct charge transfer process without changing the coordination number of iron. No intermediate complex formation was evident kinetically. Iron is in the VIIIth group of the periodic table, hence it might show a coordination number of more than six (i.e. eight) but evidence is lacking. In one of the studies in which oxidation of iodide ion was carried out with hexacyanoferrate(III), an intermediate complex with coordination number eight was assumed.[43-44]

For the first time, oxidation of a number of organic compounds by alkaline hexacyanoferrate(III) using osmium(VIII), as a homogeneous catalyst, was contributed in literature by Solymosi et. al.,[45,46] but the studies were made from analytical point of view. In 1966, Krishna and Singh[47] attempted to investigate the mechanism of the osmium tetraoxide catalysed oxidation of the alcohols with ferricyanide and found zero order kinetics in hexacyanoferrate(III) and unity with respect to alcohol and hydroxide ion. A probable mechanism showing the rapid and quantitative oxidation of osmium(VI) to osmium(VIII) with hexacyanoferrate(III) was proposed and this idea was supported by applying to other systems i.e.; by

See reference on Pg. No.12, 13

studying the oxidation of many organic compounds.

Inspite of high academic interest involved in the kinetics and mechanism of the osmium tetraoxide catalysed oxidation of organic compounds, its uses in synthetic work has drastic limitations due to its toxic character.[48] Another substitute of this catalyst is ruthenium tetraoxide which being nontoxic has an advantage over osmium tetraoxide. Some preliminary work with this has been published.[49]. It was found to attack readily a variety of functional groups and aromatic systems e.g. cyclohexane.[50] Ruthenium exists in 3 to 8 stages of valencies. Ruthenium exists in 8 valence state in ruthenium tetraoxide. Generally four state is present as its oxide which is insoluble in aqueous medium. In the year 1970, ruthenium(III) was employed as a homogeneous catalyst in alkaline ferricyanide[51] oxidation and later on more organic compounds were subjected to kinetic study using the same system. The hydride ion abstraction by ruthenium(III) from organic molecule has been suggested as rate determining step[52] and thus ruthenium(III) hydride reacts in fast step with hexacyanoferrate(III). Very recently Sriprakash. et. al.[53] have studied the kinetics of oxidation of aliphatic acids by cerium(IV) using ruthenium(III) and Ir(III) as homogeneous catalyst in sulphuric acid medium. Ruthenium(III) has also been employed in aqueous medium as catalyst to oxidise number of organic compound in combination with different oxidants like periodate and Tl(III).[54]

The choice of ferricyanide other than ammonical silver nitrate and Fehling's solution was made due to the fact as explained above. When ruthenium tetraoxide was dissolved in alkali, it was reduced to ruthenium(VI) unlike osmium tetraoxide, which on dissolution in alkali

See reference on Pg. No. 13

remains as osmium(VIII). Commercial available "$RuCl_3.xH_2O$" is known to contain some polynuclear species of Ru(VI)[55], therefore it was thought proper to start little work with ruthenium tetraoxide which is available in pure form. It is known that ruthenium tetraoxide disproportionate into perruthenate and finally to ruthenate in alkaline medium.[56] Ru(VI) in the form of ruthenate ion (RuO_4^{-2}) has been used as a homogeneous catalyst in combination with hexacyanoferrate(III) in alkaline medium to oxidise a number of organic compounds such as primary and secondary alcohols,[57-61] cyclic alcohols,[62] amines[63] and organic acids[64,65] probably for the first time. Very recently Ru(VI) catalysis in the oxidation of benzyl alcohol and its monosubstituted analogous by hexacyanoferrate(III) [Fe(III)] in t-butanol (25%, v/v) in alkaline medium has been studied.[66] The reaction is first order in [Ru(VI)], fractional order in [alcohol] and zero order each in [Fe(III)] and [base]. A mechanism involving the transfer of a hydride ion to the oxidant is suggested.

The present thesis deals with oxidation of 4-methyl-pentanol-2, 2-methoxy-ethanol, diethylene glycol, triethylene glycol and tetraethylene glycol by alkaline hexacyanoferrate(III) employing Ru(VI) as catalyst.

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CHAPTER-II

EXPERIMENTAL

2.1 MATERIAL EMPLOYED:

The compounds studied for kinetic measurements are listed below:

Compounds	Grade	Boiling Range °C
4-methyl pentanol-2	L.R. (IDPL) India	132
2-methoxy ethanol	(E. Merck) Germany	125-126
Diethylene glycol	A.R. (Pool) England	239-241.5
Triethylene glycol	(Merck) Germany	125-127
Tetraethylene glycol	A.R. (Fluka) Germany	314

All liquid compounds were distilled under reduced pressure and middle fraction was employed during the experiment. All the solutions were prepared in triple distilled water by dissolving the weighed quantity of compounds.

The other reagents used were of following grade.

Reagents	Grade
Potassium hexacyanoferrate(III)	B.D.H. (Analar)
Cerium Sulphate	L.R. (B.D.H.)
Potassium Chloride	B.D.H. (Analar)
Ferrous Ammonium Sulphate	B.D.H. (Analar)
Sodium hydroxide	G.R. (S. Merck)
Oxalic acid	B.D.H. (Analar)
Sulphuric acid	B.D.H. (Analar)
Ferroin	Centron
Sodium Perchlorate	(Merck) Germany

The solution of potassium hexacyanoferrate(III) prepared could be used only for a week, because the spectra of the hexacyanoferrate(III) solution do not alter on keeping over a week, even in diffused day light.[1]

The stock solution of cerium sulphate was prepared by the standard method.[2] This solution was diluted in sulphuric acid (2N) to check the hydrolysis and was standardised against freshly prepared solution of ferrous ammonium sulphate using ferroin as an indicator.

2.2 PREPARATION OF SODIUM RUTHENATE:

Ruthenium dioxide (Johnson Matthey & Co.) was mixed sodium periodate and little amount of distilled water was added. The whole mixture was stirred with the help of a glass rod for about three hours, sodium periodate oxidises the ruthenium(IV) into ruthenium(VIII) and thus produced ruthenium tetroxide was extracted with carbon tetrachloride (6×70 ml).

This solution was added to an equal volume of sodium hydroxide (1N). Thus ruthenium tetraoxide is converted into sodium ruthenate according to following reactions.[3]

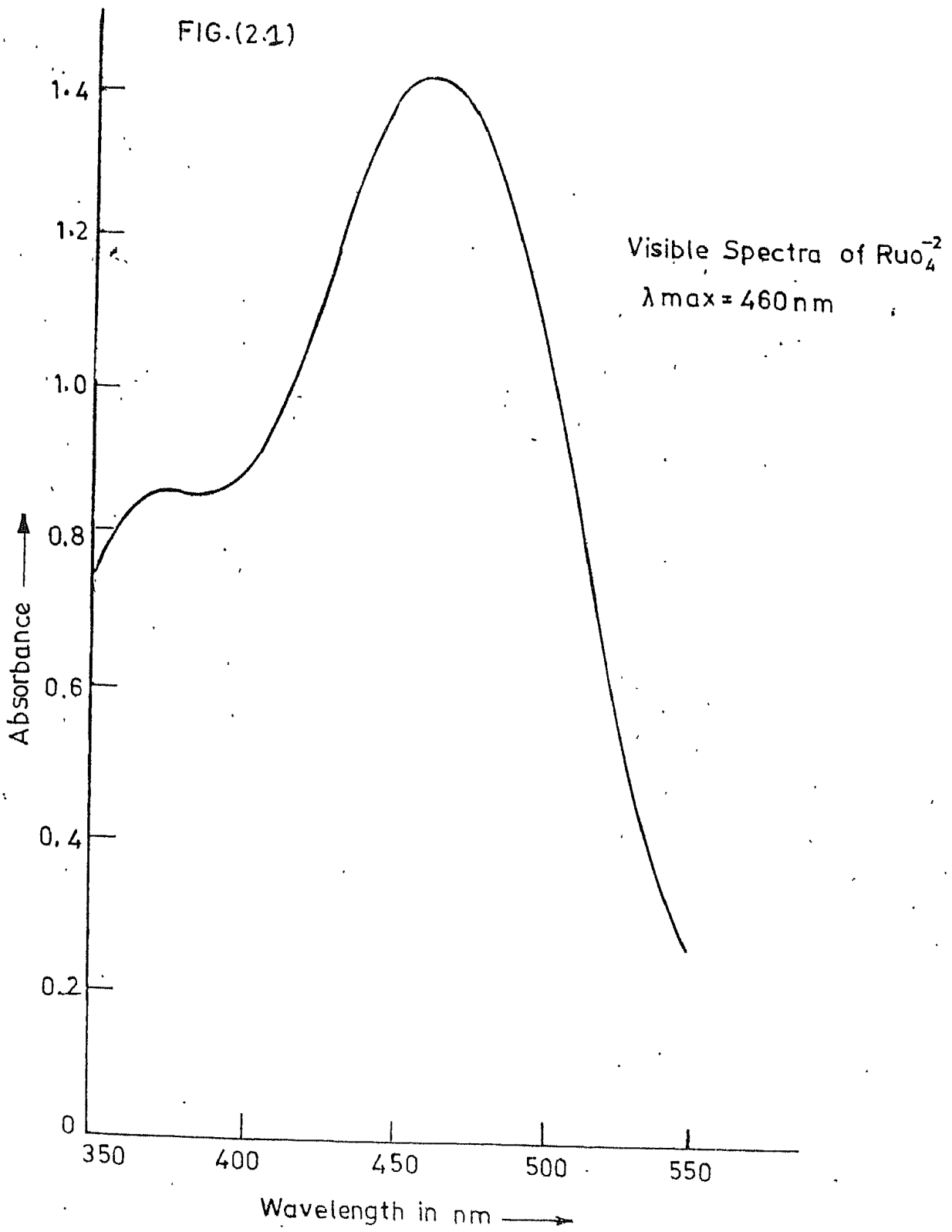
$$4RuO_4 + 4OH^- \longrightarrow 4RuO_4^- + 2H_2O + O_2\uparrow$$

$$4RuO_4^- + 4OH^- \longrightarrow 4RuO_4^{-2} + 2H_2O + O_2\uparrow$$

In order to confirm the species of ruthenium, the spectrum was recorded with the help of Beckman spectrophotometer model-220 S. Hitachi (automatic recorder) (Fig.2.1). The spectrum thus obtained was identical with the spectrum obtained by Connick and Hurley.[4] The concentration of the ruthenate ion was calculated by measuring the absorbance at 460nm; taking molar extinction coefficient[5] as 1820.

See reference on Pg. No.20

FIG.(2.1)


1.4
1.2
1.0
0.8
0.6
0.4
0.2
0
Absorbance
350
400
450
500
550
Wavelength in nm
Visible Spectra of RuO_4^{-2}
λmax = 460 nm

2.3 WORKING PROCEDURE:

All the reactions were carried out at desired temperature with the help of thermostate which could be maintained at a constant temperature with an accuracy of $\pm 0.1°C$. The calculated amount of potassium ferricyanide, sodium perchlorate, sodium hydroxide and sodium ruthenate solutions were taken in a glass stoppered flask painted with Black Japan from outside to eliminate any photochemical reaction. The solution of substrate was also kept in the same thermostate in another flask. After about an hour the requisite amount of organic substrate was pipette out into the reaction flask containing other reactants. A stop watch started just after half of the substrate solution was delivered and it was taken as zero time for the reaction. An aliquot of 5 ml. of the reaction mixture was withdrawn at different intervals of time and poured into the flask containing 5 ml. of sulphuric acid (2N) in order to quench the reaction.

The standard solution of cerium sulphate was used to estimate the hexacyanoferrate(II) produced[6] during reaction, using ferroin as an indicator. The reaction can be written as:

$$Fe(CN)_6^{-4} + Ce^{+4} \longrightarrow Fe(CN)_6^{-3} + Ce^{+3}$$

The results are reproducible within experimental error $\pm 2.0\%$.

2.4 IDENTIFICATION OF THE REACTION PRODUCTS:

The reaction flask containing potassium hexacyanoferrate(III), sodium hydroxide, sodium ruthenate and different organic substrate were kept at room temperature (25°C) for twenty four hours (concentration of hydroxyl ion is kept low). The whole mixture then neutralised with slight excess of

See reference on Pg. No.20

dilute hydrochloric acid and was shaken with ether in order to isolate the products. The ethereal layer was concentrated at water bath at 20°C. This concentrated solution was employed for identification of products in each case.

Attempts were made to identify the intermediate products but could not succeed because aldehyde were quickly oxidised to acids but in case of secondary alcohols, i.e. 4-methyl pentan-2-ol, each molecule of alcohol requires two molecules of hexacyanoferrate(III) and yield the corresponding ketone which were isolated as their D.P.H. (2,4, dinitrophenyl hydrazone) derivative m.p. 95°C.[7] (theo mp 95.5°C)

In the case of primary alcohol i.e. 2-methoxy ethanol each molecule of alcohol requires four molecules of hexacyanoferrate(III) and yield the corresponding carboxylic acid identified by paper chromatography using butanol saturated with ammonia as solvent. The final product, 2-methoxy-acetic acid in case of 2-methoxy ethanol has been identified as its Amide (mp- 95.0°C) (theo mp 96.5°C).[8,9]

In case of glycol the intermediate product its glycolaldehyde quickly oxidised to give glycolic acid. In case of di-, tri,- and tetra ethylene glycol, each molecule requires two molecules of hexacyanoferrate(III) and yield the corresponding acid i.e.; di, tri- and tetra-glycolic acid, also confirmed by spot test.[10]

Acids of this type or their derivatives, such as esters, anhydrides or imide, form dyes of the fluorescein type when melted with resorcinol, or heated with resorcinol and concentrated sulfuric acid. The dyes show a vivid green-yellow fluorescence in alkaline solution.

See reference on Pg. No.20

Organic Substrate	Final Products
1. 4-methyl pentanol-2	4-methyl pentanone-2
2. 2-methoxy ethanol	2-methoxy acetic acid.
3. 2, 2^1-dihydroxydiethyl ether	2, 2^1-dicarboxy dimethyl ether.
4. Di-β-hydroxy ethoxy ethane	2, 2^1 di-methoxy ethane dicarboxylic acid.
5. Bis-{2-(2-hydroxy ethoxy)-ethyl} ether	2, 2^1-dicarboxy dimethoxy diethyl ether

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CHAPTER-III

EXPERIMENTAL & OBSERVATIONS

3. KINETICS AND MECHANISM OF OXIDATION OF 4-METHYL PENTANOL-2, 2-METHOXY ETHANOL, DIETHYLENE GLYCOL, TRIETHYLENE GLYCOL, TETRAETHYLENE GLYCOL WITH ALKALINE HEXACYANOFERRATE(III) USING Ru(VI) AS A HOMOGENEOUS CATALYST:

The kinetic studies concerning with determination of order of the reaction with respect to each reactant provide most general method for elucidating the mechanism of a particular type of reaction. The order of reaction tells not only the rate determing step, but also throws considerable light on mechanism of the reaction.

The rate of a chemical reaction is important in determining the efficiency of many industrial reactions. In organic reactions particularly, where thee is the possibility of several reactions going on simultaneously or consecutively, the kinetic considerations will often be no less important that the equilibrium relationships.

Hence in this chapter, an attempt has been made to determine the order of the reaction with respect to each reactant under different experimental conditions and the detailed result are presented in the subsequent pages. Values in the tables marked (*) have been neglected.

3.1 DETERMINATION OF ORDER OF REACTION WITH RESPECT TO HEXACYANOFERRATE(III).

In order to determine the order of the reaction with respect to hexacyanoferrate(III), the concentration of other reactants has been kept constant except hexacyanoferrate(III). The ionic strength has been kept constant by the addition of sodium perchlorate. The reaction was followed by estimating the amount of hexacyanoferrate(II) produced at different intervals of time against the standard solution of cerium sulphate using ferroin as the redox indicator.

The first series of experiments were performed with 4-methyl pentanol-2 at constant ionic strength. Five fold range of hexacyanoferrate(III) concentration has been varied and results obtained are listed in the tables (3.1 to 3.6).

In each table the second column represents the volume of cerium sulphate solution consumed for equivalent amount of Fe(II) whereas third column represents the observed zero order rate constant values, i.e., $k_0 = \frac{\Delta x}{\Delta t}$ whereas x is the volume of cerium sulphate solution consumed for equivalent amount of hexacyanoferrate(II) produced in time t.

A persual of third column of tables (3.1 to 3.6) clearly shows that the k_0 values are fairly constant upto 60% of the reaction which clearly shows the zero order kinetics with respect to hexacyanoferrate(III) in the particular run. The graphical representation of these tables also indicates that the reaction rate follows zero order kinetics in the particular run (fig. 3.1). The zero order rate constant values has also been calculated by measuring the

slope of the straight line obtained by plotting the graph between time Vs. remaining hexacyanoferrate(III). In all figures the remaining hexacyanoferrate(III) has been expressed in terms of volume of the titrant, i.e.; cerium sulphate.

The value of k_s and (–dc/dt) are given at the foot of each table. The summarised results are given in the table (3.7). In table (3.7) the second column contains the k_s values for the particular run, obtained on multiplying the average x/t values with S/V, where S is the strength of cerium sulphate solution and V is the volume of aliquot taken each time.

Similarly the third column contains (–dc/dt) which was obtained from the slope of the plot of remaining ferricyanide Vs time (fig. 3.1). A close examination of these values of k_s and (–dc/dt) shows that they are very close to each other. The graph (fig. 3.1) clearly indicates that the reaction follows zero order kinetics with respect to hexacyanoferrate(III).

The effect of variation of hexacyanoferrate(III) concentration has again been studied by changing the concentration of alkali. The summarised results are given in the table (3.8). A close observation of tables 3.7 and 3.8 clearly shows that the k_s values increase slightly with increase in initial hexacyanoferrate(III) concentration. This has been discussed in that last chapter.

Table 3.1

Temp. = 35°C

$[K_3Fe(CN)_6]$ = 2.50×10^{-3} mol dm^{-3}

$[OH^-]$ = 1.00×10^{-1} mol dm^{-3}

[4-methyl pentanol-2] = 4.00×10^{-2} mol dm^{-3}

[Ru(VI)] = 2.18×10^{-6} mol dm^{-3}

μ = 0.25 mol dm^{-3}

Time min	$Ce(SO_4)_2$ 1.25×10^{-3}M in ml.	$k_0\times10^2$ ml min^{-1}
1	0.96	
5	1.44	12.00
10	2.04	12.00
15	2.62	11.60
20	3.20	11.60
25	3.76	11.20
30	4.32	11.20
35	4.90	11.60
40	5.46	11.20
45	6.00	10.80
50	6.40	8.00*
T_∞	10.00	

Average $k_0 = 11.40\times10^{-2}$ ml min^{-1}

A.D. = ± 2.71%

$k_s = 28.50\times10^{-6}$ mol dm^{-3} min^{-1}

$\left(-\frac{dc}{dt}\right) = 28.15\times10^{-6}$ mole dm^{-3} min^{-1}

Table 3.2

Temp. = 35°C

$[K_3Fe(CN)_6]$ = 1.66×10^{-3}mol dm^{-3}

$[OH^-]$ = 1.00×10^{-1}mol dm^{-3}

[4-methyl pentanol-2] = 4.00×10^{-2}mol dm^{-3}

[Ru(VI)] = 2.18×10^{-6}mol dm^{-3}

μ = 0.25 mol dm^{-3}

Time min	$Ce(SO_4)_2$ 1.25×10^{-3}M in ml.	$k_0\times10^2$ ml min^{-1}
1	0.92	
4	1.26	11.33
8	1.70	11.00
12	2.14	11.00
16	2.56	10.50
20	3.00	11.00
25	3.54	10.80
30	4.08	10.80
35	4.62	10.80
40	4.92	6.00*
T_∞	6.66	

Average $k_0 = 10.90\times10^{-2}$ ml min^{-1}

A.D. = ± 1.63%

$k_s = 27.25\times10^{-6}$ mol dm^{-3} min^{-1}

$\left(-\frac{dc}{dt}\right) = 28.12\times10^{-6}$ mole dm^{-3} min^{-1}

Table 3.3

Temp. = 35°C

$[K_3Fe(CN)_6]$ = 1.25×10^{-3} mol dm^{-3}

$[OH^-]$ = 1.00×10^{-1} mol dm^{-3}

[4-methyl pentanol-2] = 4.00×10^{-2} mol dm^{-3}

[Ru(VI)] = 2.18×10^{-6} mol dm^{-3}

μ = 0.25 mol dm^{-3}

Time min	$Ce(SO_4)_2$ 6.66×10^{-4}M in ml.	$k_0\times10^2$ ml min^{-1}
1	0.48	
4	1.08	20.00
7	1.68	20.00
10	2.26	19.33
13	2.84	19.33
16	3.42	19.33
19	3.98	18.66
22	4.56	19.33
25	5.12	18.66
30	5.64	10.50*
T_∞	9.30	

Average $k_0 = 19.33\times10^{-2}$ ml min^{-1}

A.D. = ± 2.12%

$k_s = 25.47\times10^{-6}$ mol dm^{-3} min^{-1}

$\left(-\frac{dc}{dt}\right) = 25.27\times10^{-6}$ mole dm^{-3} min^{-1}

Table 3.4

Temp. = 35°C

$[K_3Fe(CN)_6]$ = 1.00×10^{-3} mol dm^{-3}

$[OH^-]$ = 1.00×10^{-1} mol dm^{-3}

[4-methyl pentanol-2] = 4.00×10^{-2} mol dm^{-3}

[Ru(VI)] = 2.18×10^{-6} mol dm^{-3}

μ = 0.25 mol dm^{-3}

Time min	$Ce(SO_4)_2$ 6.66×10^{-4}M in ml.	$k_0\times10^2$ ml min^{-1}
1	0.42	
4	0.98	18.66
7	1.54	18.66
10	2.10	18.66
13	2.64	18.00
16	3.18	18.00
19	3.72	18.00
22	4.28	18.66
25	4.82	18.00
30	5.32	10.00*
T∞	6.20	

Average $k_0 = 18.40\times10^{-2}$ ml min^{-1}

A.D. = ± 1.79%

$k_s = 24.28\times10^{-6}$ mol dm^{-3} min^{-1}

$\left(-\frac{dc}{dt}\right) = 25.00\times10^{-6}$ mole dm^{-3} min^{-1}

Table 3.5

Temp. = 35°C

$[K_3Fe(CN)_6]$ = 0.66×10^{-3} mol dm^{-3}

$[OH^-]$ = 1.00×10^{-1} mol dm^{-3}

[4-methyl pentanol-2] = 4.00×10^{-2} mol dm^{-3}

[Ru(VI)] = 2.18×10^{-6} mol dm^{-3}

μ = 0.25 mol dm^{-3}

Time min	$Ce(SO_4)_2$ 4.54×10^{-4}M in ml.	$k_0\times10^2$ ml min^{-1}
1	0.52	
3	1.04	26.00
5	1.56	26.00
7	2.08	26.00
9	2.62	27.00
11	3.12	25.00
13	3.62	25.00
15	4.14	26.00
17	4.66	26.00
19	5.16	25.00
21	5.50	17.00*
T_∞	7.30	

Average $k_0 = 25.70\times10^{-2}$ ml min^{-1}

A.D. = ± 2.10%

$k_s = 23.13\times10^{-6}$ mol dm^{-3} min^{-1}

$\left(-\frac{dc}{dt}\right) = 23.40\times10^{-6}$ mole dm^{-3} min^{-1}

Table 3.6

Temp. = 35°C

$[K_3Fe(CN)_6]$ = 0.50×10^{-3} mol dm^{-3}

$[OH^-]$ = 1.00×10^{-1} mol dm^{-3}

[4-methyl pentanol-2] = 4.00×10^{-2} mol dm^{-3}

[Ru(VI)] = 2.18×10^{-6} mol dm^{-3}

μ = 0.25 mol dm^{-3}

Time min	$Ce(SO_4)_2$ 4.54×10^{-4}M in ml.	$k_0\times10^2$ ml min^{-1}
1	0.42	
2	0.66	24.00
3	0.92	26.00
4	1.18	26.00
5	1.42	24.00
6	1.66	24.00
7	1.90	24.00
8	2.16	26.00
9	2.40	24.00
10	2.64	24.00
12	2.84	20.00*
T_∞	5.50	

Average $k_0 = 24.00\times10^{-2}$ ml min^{-1}

A.D. = ± 2.75%

$k_s = 21.60\times10^{-6}$ mol dm^{-3} min^{-1}

$\left(-\frac{dc}{dt}\right) = 21.90\times10^{-6}$ mole dm^{-3} min^{-1}

Table 3.7

Temp. = 35°C
$[OH^-]$ = 1.00×10^{-1} mol dm^{-3}
[4-methyl pentanol-2] = 4.00×10^{-2} mol dm^{-3}
[Ru(VI)] = 2.18×10^{-6} mol dm^{-3}
μ = 0.25 mol dm^{-3}

$[Fe(CN)_6^{-3}]\times10^3$ mol dm^{-3}	$k_s\times10^6$ mol dm^{-3} min^{-1}	$\left(-\frac{dc}{dt}\right)\times10^6$ mol dm^{-3} min^{-1}
2.50	28.50	28.15
1.66	27.25	28.12
1.25	25.47	25.27
1.00	24.28	25.00
0.66	23.13	23.40
0.50	21.60	21.90

Table 3.8

Temp. = 35°C
$[OH^-]$ = 5.00×10^{-2} mol dm^{-3}
[4-methyl pentanol-2] = 4.00×10^{-2} mol dm^{-3}
[Ru(VI)] = 2.18×10^{-6} mol dm^{-3}
μ = 0.25 mol dm^{-3}

$[Fe(CN)_6^{-3}]\times10^3$ mol dm^{-3}	$k_s\times10^6$ mol dm^{-3} min^{-1}	$\left(-\frac{dc}{dt}\right)\times10^6$ mol dm^{-3} min^{-1}
2.50	52.50	52.05
1.66	49.00	50.00
1.25	48.84	48.34
1.00	47.52	47.02
0.66	47.02	47.22
0.50	45.00	45.64

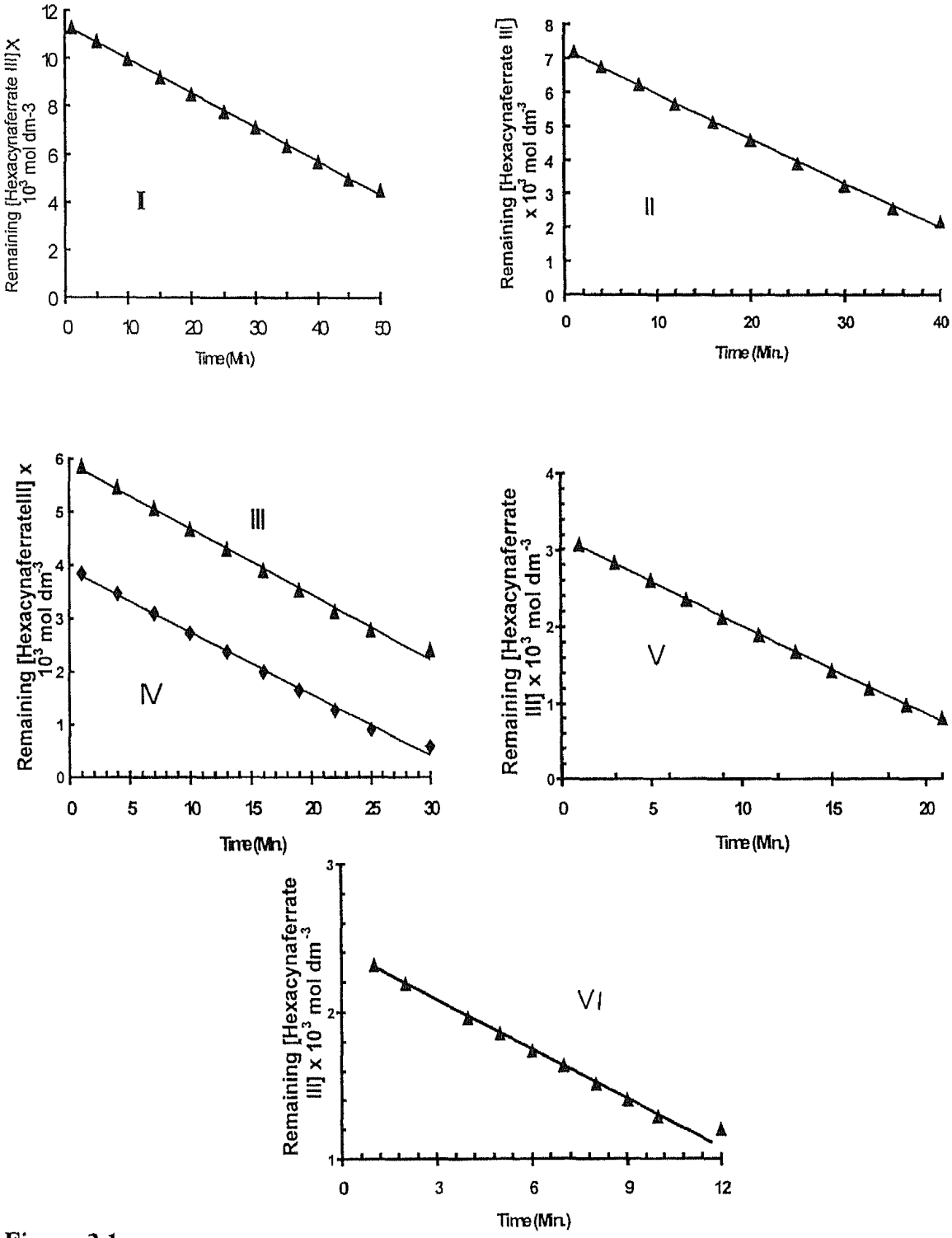


Figure 3.1

$[OH^-] = 1.00\times10^{-1}$ mol dm^{-3}; [4-Methyl Pentanol-2] = 4.00×10^{-2} mol dm^{-3}; [Ru(VI)]= 2.18×10^{-6} mol dm^{-3}, μ = 0.25 mol dm^{-3}.

$[K_3Fe(CN)_6] \times 10^3$ mol dm^{-3}			
I	2.50	IV	1.00
II	1.66	V	0.66
III	1.25	VI	0.50

The second series of experiments have been performed with 2-methoxy ethanol and the results obtained at different concentrations of hexacyanoferrate(III) are listed in the tables (3.9 to 3.14). The second column of the each table contains the concentration of hexacyanoferrate(II) in terms of volume of cerium sulphate solution and the third column contains the observed k_0 values. An close observation of these tables shows that k_0 values are fairly constant which clearly indicates the zero order kinetics with respect to hexacyanoferrate(III).

The k_s values and (–dc/dt) are given under each table. The values of (–dc/dt) are obtained from the slope of the straight lines (fig. 3.2). These straight lines have been obtained on ploting remaining ferricyanide concentration Vs time. These straight lines clearly indicates that the reaction rate follows zero order kinetics with respect to hexacyanoferrate(III). The results thus obtained are summarised in the table (3.15).

Similar results have also been obtained by changing the concentration of alkali at constant ionic strength and the results obtained are summarised in the table (3.16).

Table 3.9

Temp. = 35°C

$[K_3Fe(CN)_6]$ = 2.50×10^{-3} mol dm^{-3}

$[OH^-]$ = 1.25×10^{-1} mol dm^{-3}

[2-methoxy ethanol] = 5.00×10^{-2} mol dm^{-3}

[Ru(VI)] = 15.5×10^{-7} mol dm^{-3}

μ = 0.20 mol dm^{-3}

Time min	$Ce(SO_4)_2$ 1.00×10^{-3}M in ml.	$k_0\times10^2$ ml min^{-1}
1	0.52	
3	0.92	20.00
6	1.52	20.00
9	2.10	19.30
12	2.68	19.30
15	3.26	19.30
18	3.84	19.30
21	4.40	18.60
24	4.96	18.60
27	5.52	18.60
30	6.08	18.60
T_∞	12.5	

Average $k_0 = 19.16\times10^{-2}$ ml min^{-1}

A.D. = ± 2.60%

$k_s = 38.32\times10^{-6}$ mol dm^{-3} min^{-1}

$\left(-\frac{dc}{dt}\right) = 39.00\times10^{-6}$ mole dm^{-3} min^{-1}

Table 3.10

Temp. = 35°C

$[K_3Fe(CN)_6]$ = 1.66×10^{-3} mol dm^{-3}

$[OH^-]$ = 1.25×10^{-1} mol dm^{-3}

[2-methoxy ethanol] = 5.00×10^{-2} mol dm^{-3}

[Ru(VI)] = 15.5×10^{-7} mol dm^{-3}

μ = 0.20 mol dm^{-3}

Time min	$Ce(SO_4)_2$ 1.00×10^{-3}M in ml.	$k_0\times10^2$ ml min^{-1}
1	0.50	
3	0.86	18.00
6	1.40	18.00
9	1.94	18.00
12	2.48	18.00
15	3.00	17.30
18	3.52	17.30
21	4.04	17.30
24	4.56	17.30
27	5.06	16.60
30	5.56	16.60
T_∞	8.30	

Average $k_0 = 17.44\times10^{-2}$ ml min^{-1}

A.D. = ± 2.56%

$k_s = 34.88\times10^{-6}$ mol dm^{-3} min^{-1}

$\left(-\frac{dc}{dt}\right) = 35.18\times10^{-6}$ mole dm^{-3} min^{-1}

Table 3.11

Temp. = 35°C

$[K_3Fe(CN)_6]$ = 1.25×10^{-3} mol dm^{-3}

$[OH^-]$ = 1.25×10^{-1} mol dm^{-3}

[2-methoxy ethanol] = 5.00×10^{-2} mol dm^{-3}

[Ru(VI)] = 15.5×10^{-7} mol dm^{-3}

μ = 0.20 mol dm^{-3}

Time min	$Ce(SO_4)_2$ 0.66×10^{-3}M in ml.	$k_0\times10^2$ ml min^{-1}
1	0.54	
3	1.02	24.00
6	1.72	23.30
9	2.42	23.30
12	3.12	23.30
15	3.82	23.30
18	4.50	22.60
21	5.20	23.30
24	5.90	23.30
27	6.60	23.30
30	7.00	16.66*
T_∞	9.30	

Average $k_0 = 23.31\times10^{-2}$ ml min^{-1}

A.D. = ± 0.69%

$k_s = 30.31\times10^{-6}$ mol dm^{-3} min^{-1}

$\left(-\frac{dc}{dt}\right) = 30.80\times10^{-6}$ mole dm^{-3} min^{-1}

Table 3.12

Temp. = 35°C

$[K_3Fe(CN)_6]$ = 1.00×10^{-3} mol dm^{-3}

$[OH^-]$ = 1.25×10^{-1} mol dm^{-3}

[2-methoxy ethanol] = 5.00×10^{-2} mol dm^{-3}

[Ru(VI)] = 15.5×10^{-7} mol dm^{-3}

μ = 0.20 mol dm^{-3}

Time min	$Ce(SO_4)_2$ 0.66×10^{-3}M in ml.	$k_0\times10^2$ ml min^{-1}
1	0.52	
3	0.92	20.00
6	1.50	19.33
9	2.12	20.66
12	2.72	20.00
15	3.30	19.33
18	3.92	20.66
21	4.50	20.00
24	5.10	20.00
27	5.60	16.60*
T_∞	7.50	

Average $k_0 = 20.00\times10^{-2}$ ml min^{-1}

A.D. = ± 1.66%

$k_s = 26.40\times10^{-6}$ mol dm^{-3} min^{-1}

$\left(-\frac{dc}{dt}\right) = 26.04\times10^{-6}$ mole dm^{-3} min^{-1}

Table 3.13

Temp. = 35°C
$[K_3Fe(CN)_6]$ = 0.66×10^{-3} mol dm^{-3}
$[OH^-]$ = 1.25×10^{-1} mol dm^{-3}
[2-methoxy ethanol] = 5.00×10^{-2} mol dm^{-3}
[Ru(VI)] = 15.5×10^{-7} mol dm^{-3}
μ = 0.20 mol dm^{-3}

Time min	$Ce(SO_4)_2$ 4.54×10^{-4}M in ml.	$k_0\times10^2$ ml min^{-1}
1	0.56	
3	0.98	21.00
5	1.40	21.00
7	1.80	20.00
9	2.20	20.00
11	2.62	20.00
13	3.04	20.00
15	3.44	20.00
17	3.84	20.00
19	4.24	20.00
21	4.64	20.00
T_∞	7.30	

Average $k_0 = 20.20\times10^{-2}$ ml min^{-1}
A.D. = ± 1.58%
$k_s = 22.44\times10^{-6}$ mol dm^{-3} min^{-1}
$\left(-\frac{dc}{dt}\right) = 22.84\times10^{-6}$ mole dm^{-3} min^{-1}

Table 3.14

Temp. = 35°C
$[K_3Fe(CN)_6]$ = 0.50×10^{-3} mol dm^{-3}
$[OH^-]$ = 1.25×10^{-1} mol dm^{-3}
[2-methoxy ethanol] = 5.00×10^{-2} mol dm^{-3}
[Ru(VI)] = 15.5×10^{-7} mol dm^{-3}
μ = 0.20 mol dm^{-3}

Time min	$Ce(SO_4)_2$ 4.54×10^{-4}M in ml.	$k_0\times10^2$ ml min^{-1}
1	0.54	
3	0.90	18.00
5	1.26	18.00
7	1.60	17.00
9	1.94	17.00
11	2.30	18.00
13	2.64	17.00
15	2.98	17.00
17	3.32	17.00
19	3.66	17.00
21	3.86	10.00*
T_∞	5.50	

Average $k_0 = 17.3\times10^{-2}$ ml min^{-1}
A.D. = ± 2.50%
$k_s = 19.20\times10^{-6}$ mol dm^{-3} min^{-1}
$\left(-\frac{dc}{dt}\right) = 19.38\times10^{-6}$ mole dm^{-3} min^{-1}

Table 3.15

Temp. = 35°C
$[OH^-]$ = 1.25×10^{-1} mol dm^{-3}
[4-methoxy-ethanol] = 5.00×10^{-2} mol dm^{-3}
[Ru(VI)] = 15.5×10^{-7} mol dm^{-3}
μ = 0.20 mol dm^{-3}

$[K_3Fe(CN)_6]\times10^3$ mol dm^{-3}	$k_s\times10^6$ mol dm^{-3} min^{-1}	$\left(-\frac{dc}{dt}\right)\times10^6$ mol dm^{-3} min^{-1}
2.50	38.32	39.00
1.66	34.88	35.18
1.25	30.31	30.80
1.00	26.40	26.04
0.66	22.44	22.84
0.50	19.20	19.38

Table 3.16

Temp. = 35°C
$[OH^-]$ = 6.25×10^{-2} mol dm^{-3}
[4-methoxy-ethanol] = 5.00×10^{-2} mol dm^{-3}
[Ru(VI)] = 15.5×10^{-7} mol dm^{-3}
μ = 0.20 mol dm^{-3}

$[K_3Fe(CN)_6]\times10^3$ mol dm^{-3}	$k_s\times10^6$ mol dm^{-3} min^{-1}	$\left(-\frac{dc}{dt}\right)\times10^6$ mol dm^{-3} min^{-1}
2.50	48.84	48.64
1.66	45.85	45.24
1.25	42.36	42.84
1.00	38.08	38.48
0.66	30.80	30.18
0.50	27.52	27.82

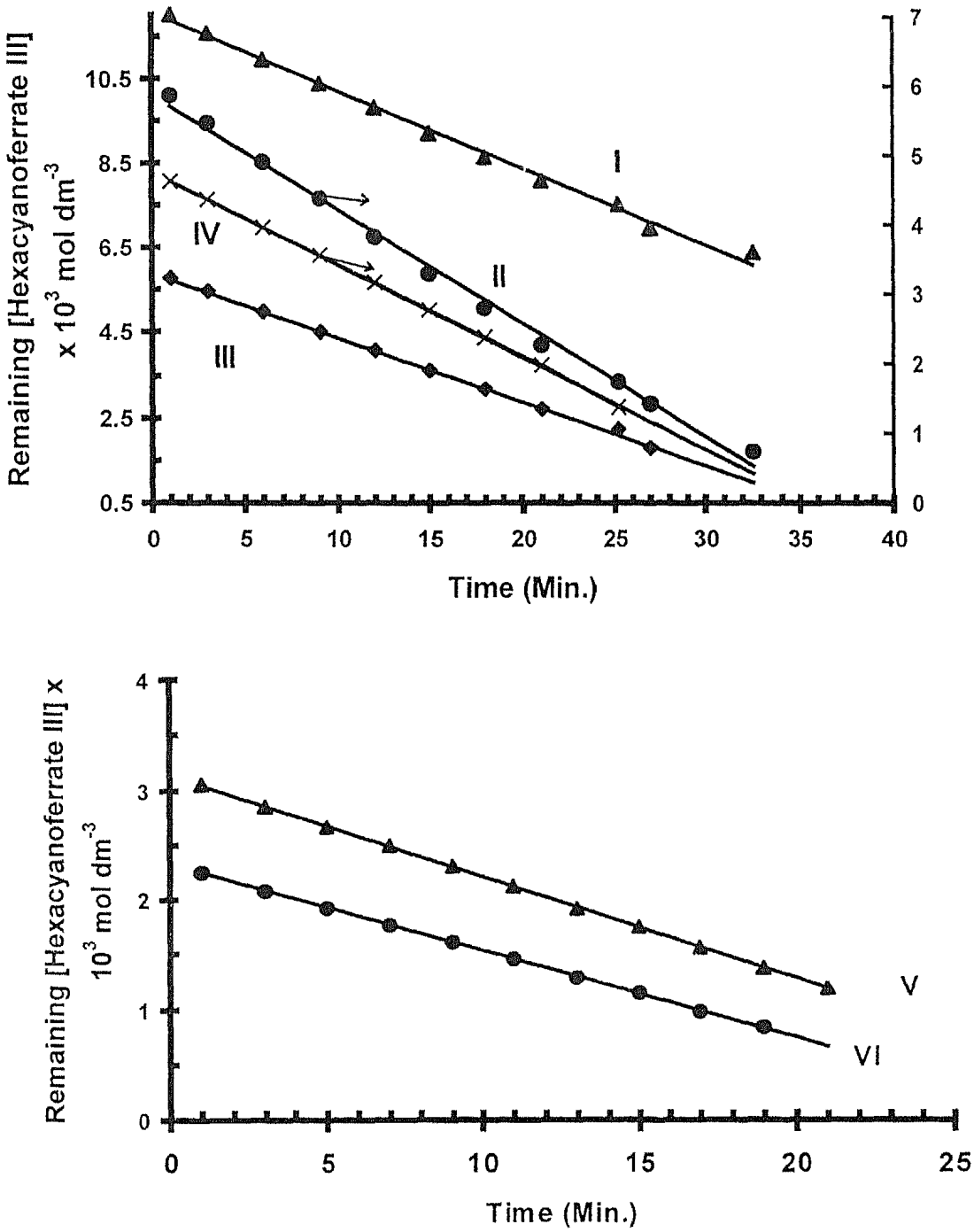


Figure 3.2 $[OH^-] = 1.25\times10^{-1}$ mol dm^{-3}; [2-Methoxy Ethanol] = 5.00×10^{-2} mol dm^{-3}; [Ru(VI)]= 15.5×10^{-7} mol dm^{-3}, $\mu = 0.20$ mol dm^{-3}.

	$[K_3Fe(CN)_6] \times 10^3$ mol dm^{-3}		
I	2.50	IV	1.00
II	1.66	V	0.66
III	1.25	VI	0.50

The third series of experiments have been performed with diethylene glycol and the results obtained at different concentration of hexacyanoferrate(III) are listed in the tables (3.17 to 3.22). The second column of each table contains the concentration of hexacyanoferrate(III) in terms of volume of cerium sulphate solution and the third column contains the observed k_0 values. An close observation of these tables shows that k_0 values are fairly constant which clearly indicates the zero order kinetics with respect to hexacyanoferrate(III).

The k_s values and (–dc/dt) are given under each tables. The values of (–dc/dt) are obtained from the slope of the straight lines (fig. 3.3). These straight lines have been obtained on plotting remaining ferricyanide concentration Vs time. These straight lines clearly indicates that the reaction rate follows zero order kinetics with respect of hexacyanoferrate(III). The results thus obtained are summarised in the table (3.23).

Similar results have been obtained by changing the concentration of the substrate at constant ionic strength and the results obtained are summarised in table (3.24).

Table 3.17

Temp. = 30°C

$[K_3Fe(CN)_6]$ = 2.50×10^{-3} mol dm^{-3}

$[OH^-]$ = 1.00×10^{-1} mol dm^{-3}

[Diethylene glycol] = 2.00×10^{-2} mol dm^{-3}

[Ru(VI)] = 3.66×10^{-6} mol dm^{-3}

μ = 0.25 mol dm^{-3}

Time min	$Ce(SO_4)_2$ 1.00×10^{-3}M in ml.	$k_0\times10^2$ ml min^{-1}
1	0.28	
5	0.64	9.00
10	1.08	8.80
15	1.50	8.40
20	1.96	9.20
25	2.38	8.40
30	2.84	9.20
35	3.30	8.80
40	3.74	8.80
45	4.18	8.80
50	4.62	8.80
T_∞	12.50	

Average $k_0 = 8.86\times10^{-2}$ ml min^{-1}

A.D. = ± 2.30%

$k_s = 17.72\times10^{-6}$ mol dm^{-3} min^{-1}

$\left(-\frac{dc}{dt}\right) = 18.00\times10^{-6}$ mole dm^{-3} min^{-1}

Table 3.18

Temp. = 30°C

$[K_3Fe(CN)_6]$ = 1.66×10^{-3} mol dm^{-3}

$[OH^-]$ = 1.00×10^{-1} mol dm^{-3}

[Diethylene glycol] = 2.00×10^{-2} mol dm^{-3}

[Ru(VI)] = 3.66×10^{-6} mol dm^{-3}

μ = 0.25 mol dm^{-3}

Time min	$Ce(SO_4)_2$ 1.00×10^{-3}M in ml.	$k_0\times10^2$ ml min^{-1}
1	0.28	
5	0.60	8.00
10	0.98	7.60
15	1.36	7.60
20	1.76	8.00
25	2.16	8.00
30	2.58	8.40
35	2.96	7.60
40	3.34	7.60
45	3.70	7.20
50	4.06	7.20
T_∞	8.30	

Average $k_0 = 7.72\times10^{-2}$ ml min^{-1}

A.D. = ± 3.93%

$k_s = 15.44\times10^{-6}$ mol dm^{-3} min^{-1}

$\left(-\frac{dc}{dt}\right) = 15.74\times10^{-6}$ mole dm^{-3} min^{-1}

Table 3.19

Temp. = 30°C

$[K_3Fe(CN)_6]$ = 1.25×10^{-3} mol dm^{-3}

$[OH^-]$ = 1.00×10^{-1} mol dm^{-3}

[Diethylene glycol] = 2.00×10^{-2} mol dm^{-3}

[Ru(VI)] = 3.66×10^{-6} mol dm^{-3}

μ = 0.25 mol dm^{-3}

Time min	$Ce(SO_4)_2$ 1.00×10^{-3}M in ml.	$k_0\times10^2$ ml min^{-1}
1	0.30	
5	0.60	7.28
10	0.94	6.80
15	1.36	8.40
20	1.72	7.20
25	2.06	6.80
30	2.40	6.80
35	2.74	6.80
40	3.10	7.20
45	3.44	6.80
50	3.78	6.80
T_∞	6.25	

Average $k_0 = 7.08\times10^{-2}$ ml min^{-1}

A.D. = ± 2.09%

$k_s = 14.17\times10^{-6}$ mol dm^{-3} min^{-1}

$\left(-\frac{dc}{dt}\right) = 14.87\times10^{-6}$ mole dm^{-3} min^{-1}

Table 3.20

Temp. = 30°C

$[K_3Fe(CN)_6]$ = 1.00×10^{-3} mol dm^{-3}

$[OH^-]$ = 1.00×10^{-1} mol dm^{-3}

[Diethylene glycol] = 2.00×10^{-2} mol dm^{-3}

[Ru(VI)] = 3.66×10^{-6} mol dm^{-3}

μ = 0.25 mol dm^{-3}

Time min	$Ce(SO_4)_2$ 4.54×10^{-4}M in ml.	$k_0\times10^2$ ml min^{-1}
1	0.32	
5	0.82	12.5
10	1.44	12.4
15	2.06	12.4
20	2.66	12.0
25	3.26	12.0
30	3.88	12.4
35	4.48	12.0
40	5.06	11.6
45	5.64	11.6
50	6.24	12.0
T_∞	11.00	

Average $k_0 = 12.09\times10^{-2}$ ml min^{-1}

A.D. = ± 2.21%

$k_s = 10.88\times10^{-6}$ mol dm^{-3} min^{-1}

$\left(-\frac{dc}{dt}\right) = 10.28\times10^{-6}$ mole dm^{-3} min^{-1}

Table 3.21

Temp. = 30°C

$[K_3Fe(CN)_6]$ = 0.66×10^{-3} mol dm^{-3}

$[OH^-]$ = 1.00×10^{-1} mol dm^{-3}

[Diethylene glycol] = 2.00×10^{-2} mol dm^{-3}

[Ru(VI)] = 3.66×10^{-6} mol dm^{-3}

μ = 0.25 mol dm^{-3}

Time min	$Ce(SO_4)_2$ 4.54×10^{-4}M in ml.	$k_0\times10^2$ ml min^{-1}
1	0.30	
5	0.68	9.50
10	1.16	9.60
15	1.62	9.20
20	2.08	9.20
25	2.52	8.80
30	2.98	9.20
35	3.44	9.20
40	3.90	9.20
45	4.34	8.80
50	4.78	8.80
T_∞	7.30	

Average $k_0 = 9.15\times10^{-2}$ ml min^{-1}

A.D. = ± 2.40%

$k_s = 8.23\times10^{-6}$ mol dm^{-3} min^{-1}

$\left(-\frac{dc}{dt}\right) = 8.64\times10^{-6}$ mole dm^{-3} min^{-1}

Table 3.22

Temp. = 30°C

$[K_3Fe(CN)_6]$ = 0.50×10^{-3} mol dm^{-3}

$[OH^-]$ = 1.00×10^{-1} mol dm^{-3}

[Diethylene glycol] = 2.00×10^{-2} mol dm^{-3}

[Ru(VI)] = 3.66×10^{-6} mol dm^{-3}

μ = 0.25 mol dm^{-3}

Time min	$Ce(SO_4)_2$ 4.54×10^{-4}M in ml.	$k_0\times10^2$ ml min^{-1}
1	0.30	
5	0.64	8.50
10	1.08	8.80
15	1.50	8.40
20	1.92	8.40
25	2.32	8.00
30	2.72	8.00
35	3.14	8.40
40	3.54	8.00
45	3.92	7.60
50	4.20	5.60*
T_∞	5.50	

Average $k_0 = 8.24\times10^{-2}$ ml min^{-1}

A.D. = ± 3.58%

$k_s = 7.41\times10^{-6}$ mol dm^{-3} min^{-1}

$\left(-\frac{dc}{dt}\right) = 7.48\times10^{-6}$ mole dm^{-3} min^{-1}

Table 3.23

Temp. = 30°C
$[OH^-]$ = 1.00×10^{-1} mol dm^{-3}
[Diethylene glycol] = 2.00×10^{-2} mol dm^{-3}
[Ru(VI)] = 3.66×10^{-6} mol dm^{-3}
μ = 0.25 mol dm^{-3}

$[K_3Fe(CN)_6]\times10^3$ mol dm^{-3}	$k_s\times10^6$ mol dm^{-3} min^{-1}	$\left(-\frac{dc}{dt}\right)\times10^6$ mol dm^{-3} min^{-1}
2.50	17.72	18.00
1.66	15.44	15.74
1.25	14.17	14.87
1.00	10.88	10.28
0.66	8.23	8.64
0.50	7.41	7.48

Table 3.24

Temp. = 30°C
$[OH^-]$ = 1.00×10^{-1} mol dm^{-3}
[Diethylene glycol] = 4.00×10^{-2} mol dm^{-3}
[Ru(VI)] = 3.66×10^{-6} mol dm^{-3}
μ = 0.25 mol dm^{-3}

$[K_3Fe(CN)_6]\times10^3$ mol dm^{-3}	$k_s\times10^6$ mol dm^{-3} min^{-1}	$\left(-\frac{dc}{dt}\right)\times10^6$ mol dm^{-3} min^{-1}
2.50	38.32	38.82
1.66	34.68	34.18
1.25	33.46	33.36
1.00	30.96	30.06
0.66	25.26	25.97
0.50	24.82	23.14

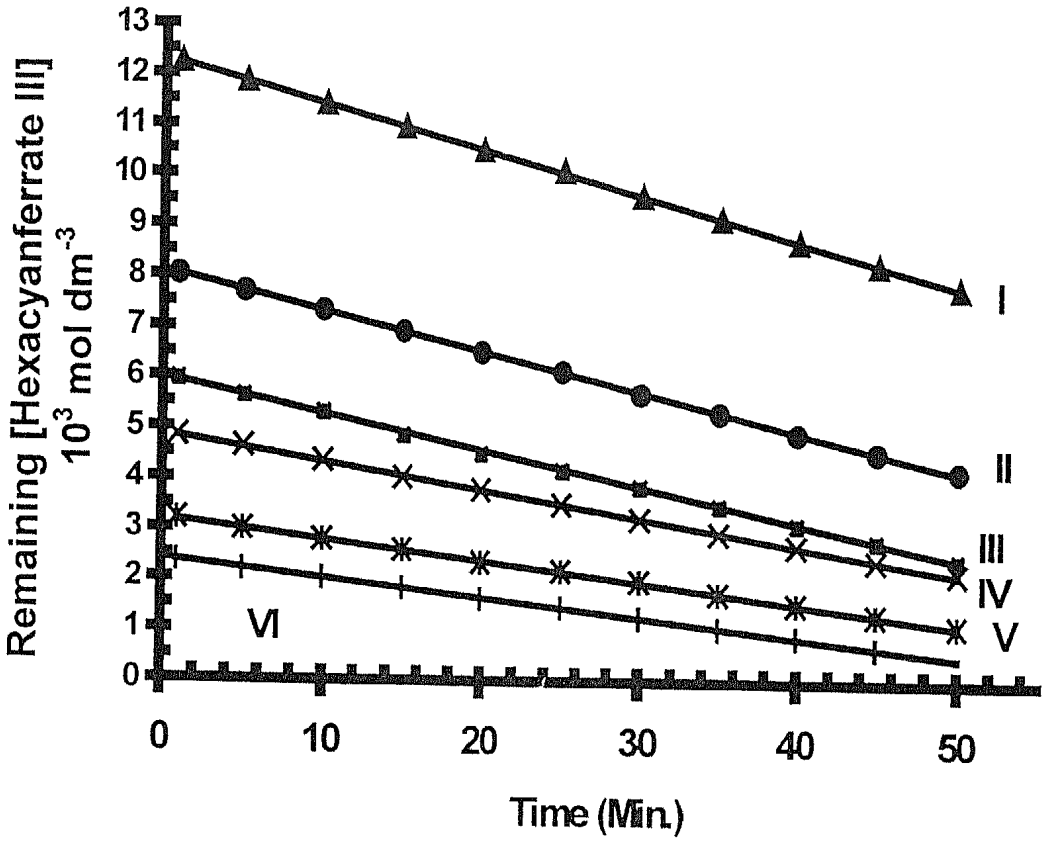


Figure 3.3 $[OH^-] = 1.00\times10^{-1}$ mol dm^{-3}; [Diethylene Glycol] $= 2.00\times10^{-2}$ mol dm^{-3}; [Ru(VI)]$= 3.66\times10^{-6}$ mol dm^{-3}, $\mu = 0.25$ mol dm^{-3}.

	$[K_3Fe(CN)_6] \times 10^3$ mol dm^{-3}
I	2.50
II	1.66
III	1.25
IV	1.00
V	0.66
VI	0.50

The fourth series of experiments have been performed with triethylene glycol and the results obtained at various concentration of hexacyanoferrate(III) are listed in the tables (3.25 to 3.30). The average k_0, k_5 and (–dc/dt) values are given below in each table.

A careful observation of the tables (3.25 to 3.30) clearly indicates that the values of k_0 are fairly constant and confirm the zero order kinetics. The summarised result are given in the table (3.31 and 3.32) clearly shows the zero order kinetics with respect to hexacyanoferrate(III). Table (3.32) contains the summarised results obtained by studying the reaction at different concentration of the substrate.

Table 3.25

Temp. = 35°C

$[K_3Fe(CN)_6]$ = 2.50×10^{-3} mol dm^{-3}

$[OH^-]$ = 1.00×10^{-1} mol dm^{-3}

[Triethylene glycol] = 2.00×10^{-2} mol dm^{-3}

[Ru(VI)] = 4.8×10^{-6} mol dm^{-3}

μ = 0.20 mol dm^{-3}

Time min	$Ce(SO_4)_2$ 1.25×10^{-3}M in ml.	$k_0\times10^2$ ml min^{-1}
1	0.56	
3	0.76	10.00
6	1.06	10.00
9	1.36	10.00
12	1.66	10.00
15	1.94	9.30
20	2.50	11.20
25	3.04	10.80
30	3.52	9.60
35	4.00	9.60
40	4.50	10.00
T_∞	10.00	

Average $k_0 = 10.05\times10^{-2}$ ml min^{-1}

A.D. = ± 3.03%

$k_s = 25.1\times10^{-6}$ mol dm^{-3} min^{-1}

$\left(-\frac{dc}{dt}\right) = 25.81\times10^{-6}$ mole dm^{-3} min^{-1}

Table 3.26

Temp. = 35°C

$[K_3Fe(CN)_6]$ = 1.66×10^{-3} mol dm^{-3}

$[OH^-]$ = 1.00×10^{-1} mol dm^{-3}

[Triethylene glycol] = 2.00×10^{-2} mol dm^{-3}

[Ru(VI)] = 4.8×10^{-6} mol dm^{-3}

μ = 0.20 mol dm^{-3}

Time min	$Ce(SO_4)_2$ 1.25×10^{-3}M in ml.	$k_0\times10^2$ ml min^{-1}
1	0.50	
5	0.90	10.00
10	1.38	9.60
15	1.86	9.60
20	2.34	9.60
25	2.82	9.60
30	3.28	9.20
35	3.76	9.60
40	4.22	9.20
45	4.62	8.00*
T_∞	6.66	

Average $k_0 = 9.55\times10^{-2}$ ml min^{-1}

A.D. = ± 1.83%

$k_s = 23.87\times10^{-6}$ mol dm^{-3} min^{-1}

$\left(-\frac{dc}{dt}\right) = 23.07\times10^{-6}$ mole dm^{-3} min^{-1}

Table 3.27

Temp. = 35°C

$[K_3Fe(CN)_6]$ = 1.25×10^{-3} mol dm^{-3}

$[OH^-]$ = 1.00×10^{-1} mol dm^{-3}

[Triethylene glycol] = 2.00×10^{-2} mol dm^{-3}

[Ru(VI)] = 4.8×10^{-6} mol dm^{-3}

μ = 0.20 mol dm^{-3}

Time min	$Ce(SO_4)_2$ 8.33×10^{-4}M in ml.	$k_0\times10^2$ ml min^{-1}
1	0.64	
5	1.12	12.00
10	1.74	12.40
15	2.36	12.40
20	3.00	12.80
25	3.62	12.40
30	4.22	12.00
35	4.84	12.40
40	5.44	12.00
45	6.00	11.00*
T_∞	7.50	

Average $k_0 = 12.3\times10^{-2}$ ml min^{-1}

A.D. = ± 1.82%

$k_s = 20.41\times10^{-6}$ mol dm^{-3} min^{-1}

$\left(-\frac{dc}{dt}\right) = 21.00\times10^{-6}$ mole dm^{-3} min^{-1}

Table 3.28

Temp. = 35°C

$[K_3Fe(CN)_6]$ = 1.00×10^{-3} mol dm^{-3}

$[OH^-]$ = 1.00×10^{-1} mol dm^{-3}

[Triethylene glycol] = 2.00×10^{-2} mol dm^{-3}

[Ru(VI)] = 4.8×10^{-6} mol dm^{-3}

μ = 0.20 mol dm^{-3}

Time min	$Ce(SO_4)_2$ 8.33×10^{-4}M in ml.	$k_0\times10^2$ ml min^{-1}
1	0.70	
3	0.92	11.00
6	1.26	11.30
9	1.60	11.30
12	1.90	11.30
15	2.24	11.30
20	2.82	11.60
25	3.38	11.20
30	3.94	11.20
35	4.50	11.20
T_∞	6.00	

Average $k_0 = 11.26\times10^{-2}$ ml min^{-1}

A.D. = ± 0.92%

$k_s = 18.67\times10^{-6}$ mol dm^{-3} min^{-1}

$\left(-\frac{dc}{dt}\right) = 18.06\times10^{-6}$ mole dm^{-3} min^{-1}

Table 3.29

Temp. = 35°C

$[K_3Fe(CN)_6]$ = 0.66×10^{-3} mol dm^{-3}

$[OH^-]$ = 1.00×10^{-1} mol dm^{-3}

[Triethylene glycol] = 2.00×10^{-2} mol dm^{-3}

[Ru(VI)] = 4.8×10^{-6} mol dm^{-3}

μ = 0.20 mol dm^{-3}

Time min	$Ce(SO_4)_2$ 4.54×10^{-4}M in ml.	$k_0\times10^2$ ml min^{-1}
1	0.74	
3	1.12	19.00
6	1.70	19.30
9	2.28	19.30
12	2.86	19.30
15	3.42	18.60
18	3.98	18.60
21	4.54	18.60
24	5.12	19.30
27	5.68	18.60
T_∞	7.30	

Average $k_0 = 18.95\times10^{-2}$ ml min^{-1}

A.D. = ± 1.66%

$k_s = 17.05\times10^{-6}$ mol dm^{-3} min^{-1}

$\left(-\frac{dc}{dt}\right) = 17.85\times10^{-6}$ mole dm^{-3} min^{-1}

Table 3.30

Temp. = 35°C

$[K_3Fe(CN)_6]$ = 0.50×10^{-3} mol dm^{-3}

$[OH^-]$ = 1.00×10^{-1} mol dm^{-3}

[Triethylene glycol] = 2.00×10^{-2} mol dm^{-3}

[Ru(VI)] = 4.8×10^{-6} mol dm^{-3}

μ = 0.20 mol dm^{-3}

Time min	$Ce(SO_4)_2$ 4.54×10^{-4}M in ml.	$k_0\times10^2$ ml min^{-1}
1	0.76	
3	1.14	19.00
5	1.50	18.00
7	1.86	18.00
9	2.22	18.00
11	2.60	19.00
13	2.96	18.00
15	3.32	18.00
17	3.68	18.00
19	3.98	15.00*
T_∞	5.50	

Average $k_0 = 18.25\times10^{-2}$ ml min^{-1}

A.D. = ± 2.05%

$k_s = 16.42\times10^{-6}$ mol dm^{-3} min^{-1}

$\left(-\frac{dc}{dt}\right) = 17.00\times10^{-6}$ mole dm^{-3} min^{-1}

Table 3.31

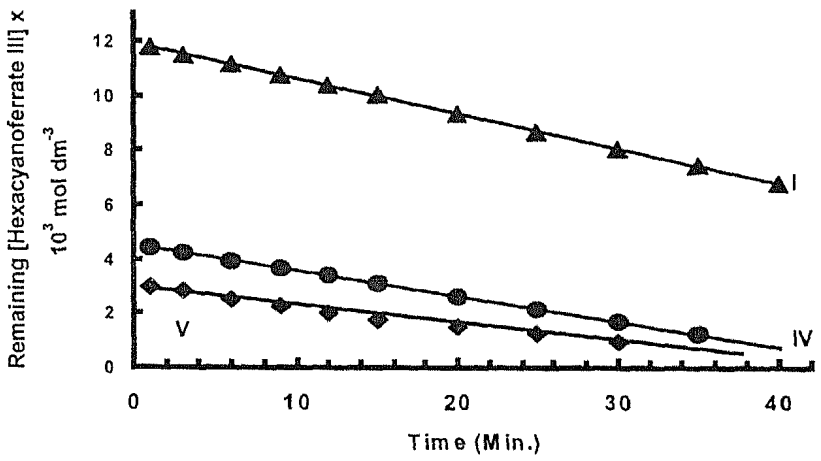
Temp. = 35°C
$[OH^-]$ = 1.00×10^{-1} mol dm^{-3}
[Triethylene glycol] = 2.00×10^{-2} mol dm^{-3}
[Ru(VI)] = 4.8×10^{-6} mol dm^{-3}
μ = 0.20 mol dm^{-3}

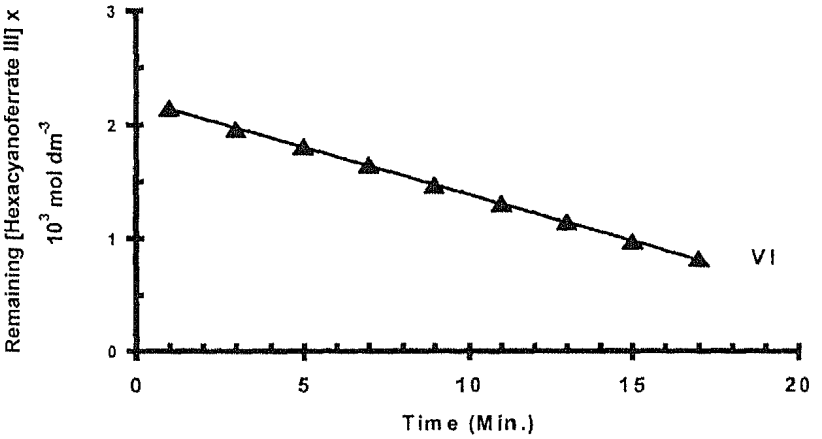
$[K_3Fe(CN)_6]\times10^3$ mol dm^{-3}	$k_s\times10^6$ mol dm^{-3} min^{-1}	$\left(-\frac{dc}{dt}\right)\times10^6$ mol dm^{-3} min^{-1}
2.50	25.10	25.81
1.66	23.87	23.07
1.25	20.41	21.00
1.00	18.67	18.06
0.66	17.05	17.85
0.50	16.42	17.00

Table 3.32

Temp. = 35°C
$[OH^-]$ = 1.00×10^{-2} mol dm^{-3}
[Triethylene glycol] = 4.00×10^{-2} mol dm^{-3}
[Ru(VI)] = 4.8×10^{-6} mol dm^{-3}
μ = 0.20 mol dm^{-3}

$[K_3Fe(CN)_6]\times10^3$ mol dm^{-3}	$k_s\times10^6$ mol dm^{-3} min^{-1}	$\left(-\frac{dc}{dt}\right)\times10^6$ mol dm^{-3} min^{-1}
2.50	39.33	40.00
1.66	36.77	37.17
1.25	34.42	35.10
1.00	32.86	32.06
0.66	31.50	32.00
0.50	31.00	31.86





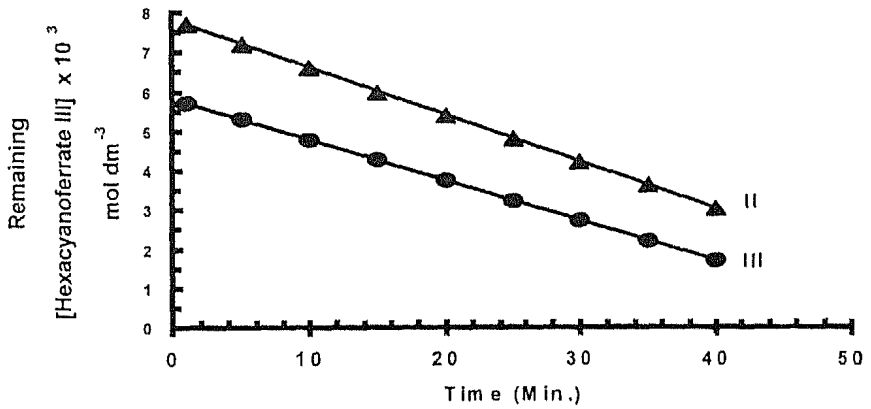


Figure 3.4 $[OH^-] = 1.00\times10^{-1}$ mol dm^{-3}; [Triethylene Glycol] $= 2.00\times10^{-2}$ mol dm^{-3}; [Ru(VI)]$= 4.88\times10^{-6}$ mol dm^{-3}, $\mu = 0.20$ mol dm^{-3}.

	$[K_3Fe(CN)_6] \times 10^3$ mol dm^{-3}		
I	2.50	IV	1.00
II	1.66	V	0.66
III	1.25	VI	0.50

The fifth and the last series of experiments have been performed with tetraethylene glycol, and results obtained at concentration of hexacyanoferrate(III) are listed in the tables (3.33 to 3.39). The average k_0, k_s, (–dc/dt) values are given below in each table.

A careful observation of the table (3.33 to 3.38) clearly indicates that the values of k_0 are fairly constant and confirm the zero order kinetics the particular run most of the tables have also been reproduced in the form of the graph (fig. 3.5) which clearly shows that the reaction is zero order with respect to hexacyanoferrate(III). The summarised results are given in the tables (3.39 to 3.40) clearly shows the zero order kinetics with respect to hexacyanoferrate(III). Table (3.40) contains the summarised results obtained by studying the reaction at different concentration of the substrate.

Table 3.33

Temp. = 35°C

$[K_3Fe(CN)_6]$ = 2.50×10^{-3} mol dm^{-3}

$[OH^-]$ = 1.00×10^{-1} mol dm^{-3}

[Tetraethylene glycol] = 2.50×10^{-2} mol dm^{-3}

[Ru(VI)] = 6.55×10^{-6} mol dm^{-3}

μ = 0.20 mol dm^{-3}

Time min	$Ce(SO_4)_2$ 1.00×10^{-3}M in ml.	$k_0\times10^2$ ml min^{-1}
1	0.38	
5	0.76	9.50
10	1.24	9.60
15	1.72	9.60
20	2.18	9.20
25	2.64	9.20
30	3.12	9.60
35	3.58	9.20
40	4.04	9.20
45	4.50	9.20
50	4.96	9.20
T_∞	12.50	

Average $k_0 = 9.35\times10^{-2}$ ml min^{-1}

A.D. = ± 1.92%

$k_s = 18.70\times10^{-6}$ mol dm^{-3} min^{-1}

$\left(-\frac{dc}{dt}\right) = 18.95\times10^{-6}$ mole dm^{-3} min^{-1}

Table 3.34

Temp. = 35°C

$[K_3Fe(CN)_6]$ = 1.66×10^{-3} mol dm^{-3}

$[OH^-]$ = 1.00×10^{-1} mol dm^{-3}

[Tetraethylene glycol] = 2.50×10^{-2} mol dm^{-3}

[Ru(VI)] = 6.55×10^{-6} mol dm^{-3}

μ = 0.20 mol dm^{-3}

Time min	$Ce(SO_4)_2$ 1.00×10^{-3}M in ml.	$k_0\times10^2$ ml min^{-1}
1	0.36	
5	0.72	9.00
10	1.18	9.20
15	1.62	8.80
20	2.06	8.80
25	2.50	8.80
30	2.96	9.20
35	3.40	8.80
40	3.86	8.80
45	4.30	8.80
50	4.72	8.40
T_∞	8.30	

Average $k_0 = 8.86\times10^{-2}$ ml min^{-1}

A.D. = ± 1.85%

$k_s = 17.72\times10^{-6}$ mol dm^{-3} min^{-1}

$\left(-\frac{dc}{dt}\right) = 17.50\times10^{-6}$ mole dm^{-3} min^{-1}

Table 3.35

Temp. = 35°C

$[K_3Fe(CN)_6]$ = 1.25×10^{-3} mol dm^{-3}

$[OH^-]$ = 1.00×10^{-1} mol dm^{-3}

[Tetraethylene glycol] = 2.50×10^{-2} mol dm^{-3}

[Ru(VI)] = 6.55×10^{-6} mol dm^{-3}

μ = 0.20 mol dm^{-3}

Time min	$Ce(SO_4)_2$ 6.66×10^{-4}M in ml.	$k_0\times10^2$ ml min^{-1}
1	0.48	
5	0.96	12.00
10	1.56	12.00
15	2.16	12.00
20	2.78	12.40
25	3.38	12.00
30	4.02	12.80
35	4.64	12.40
40	5.24	12.00
45	5.84	12.00
50	6.42	11.60
T_∞	9.30	

Average $k_0 = 12.12\times10^{-2}$ ml min^{-1}

A.D. = ± 2.04%

$k_s = 15.99\times10^{-6}$ mol dm^{-3} min^{-1}

$\left(-\frac{dc}{dt}\right) = 16.12\times10^{-6}$ mole dm^{-3} min^{-1}

Table 3.36

Temp. = 35°C

$[K_3Fe(CN)_6]$ = 1.00×10^{-3} mol dm^{-3}

$[OH^-]$ = 1.00×10^{-1} mol dm^{-3}

[Tetraethylene glycol] = 2.50×10^{-2} mol dm^{-3}

[Ru(VI)] = 6.55×10^{-6} mol dm^{-3}

μ = 0.20 mol dm^{-3}

Time min	$Ce(SO_4)_2$ 6.66×10^{-4}M in ml.	$k_0\times10^2$ ml min^{-1}
1	0.48	
5	0.96	12.00
10	1.54	11.60
15	2.10	11.20
20	2.70	12.00
25	3.28	11.60
30	3.86	11.60
35	4.42	11.20
40	4.98	11.20
45	5.52	10.80
50	5.82	6.00*
T_∞	7.50	

Average $k_0 = 11.46\times10^{-2}$ ml min^{-1}

A.D. = ± 3.31%

$k_s = 15.12\times10^{-6}$ mol dm^{-3} min^{-1}

$\left(-\frac{dc}{dt}\right) = 15.40\times10^{-6}$ mole dm^{-3} min^{-1}

Table 3.37

Temp. = 35°C

$[K_3Fe(CN)_6]$ = 6.66×10^{-4} mol dm^{-3}

$[OH^-]$ = 1.00×10^{-1} mol dm^{-3}

[Tetraethylene glycol] = 2.50×10^{-2} mol dm^{-3}

[Ru(VI)] = 6.55×10^{-6} mol dm^{-3}

μ = 0.20 mol dm^{-3}

Time min	$Ce(SO_4)_2$ 4.54×10^{-4}M in ml.	$k_0\times10^2$ ml min^{-1}
1	0.52	
3	0.82	15.00
6	1.24	14.00
9	1.68	14.60
12	2.10	14.00
15	2.50	13.30
18	2.92	14.00
21	3.34	14.00
24	3.76	14.00
27	4.16	13.30
30	4.56	13.30
T_∞	7.30	

Average $k_0 = 13.95\times10^{-2}$ ml min^{-1}

A.D. = ± 2.79%

$k_s = 12.55\times10^{-6}$ mol dm^{-3} min^{-1}

$\left(-\frac{dc}{dt}\right) = 12.85\times10^{-6}$ mole dm^{-3} min^{-1}

Table 3.38

Temp. = 35°C

$[K_3Fe(CN)_6]$ = 5.00×10^{-4} mol dm^{-3}

$[OH^-]$ = 1.00×10^{-1} mol dm^{-3}

[Tetraethylene glycol] = 2.50×10^{-2} mol dm^{-3}

[Ru(VI)] = 6.55×10^{-6} mol dm^{-3}

μ = 0.20 mol dm^{-3}

Time min	$Ce(SO_4)_2$ 4.54×10^{-4}M in ml.	$k_0\times10^2$ ml min^{-1}
1	0.50	
3	0.92	12.00
6	1.32	13.33
9	1.72	13.33
12	2.10	12.60
15	2.48	12.60
18	2.86	12.60
21	3.22	12.00
24	3.58	12.00
27	3.92	11.33
30	4.12	6.60*
T_∞	5.50	

Average $k_0 = 12.41\times10^{-2}$ ml min^{-1}

A.D. = ± 4.19%

$k_s = 11.16\times10^{-6}$ mol dm^{-3} min^{-1}

$\left(-\frac{dc}{dt}\right) = 12.02\times10^{-6}$ mole dm^{-3} min^{-1}

Table 3.39

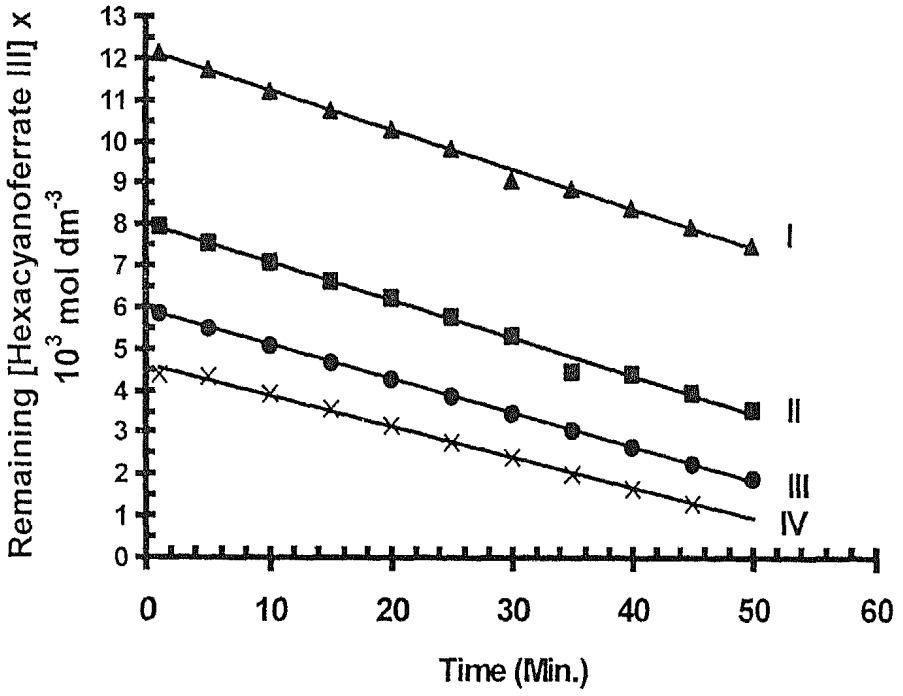
Temp. = 35°C
$[OH^-]$ = 1.00×10^{-1} mol dm^{-3}
[Tetraethylene glycol] = 2.50×10^{-2} mol dm^{-3}
[Ru(VI)] = 6.55×10^{-6} mol dm^{-3}
μ = 0.20 mol dm^{-3}

$[K_3Fe(CN)_6]\times10^3$ mol dm^{-3}	$k_s\times10^6$ mol dm^{-3} min^{-1}	$\left(-\frac{dc}{dt}\right)\times10^6$ mol dm^{-3} min^{-1}
2.50	18.70	19.00
1.66	17.72	18.00
1.25	15.99	16.00
1.00	15.12	15.00
0.66	12.55	12.10
0.50	11.16	10.98

Table 3.40

Temp. = 35°C
$[OH^-]$ = 1.00×10^{-1} mol dm^{-3}
[Tetraethylene glycol] = 5.00×10^{-2} mol dm^{-3}
[Ru(VI)] = 6.55×10^{-6} mol dm^{-3}
μ = 0.20 mol dm^{-3}

$[K_3Fe(CN)_6]\times10^3$ mol dm^{-3}	$k_s\times10^6$ mol dm^{-3} min^{-1}	$\left(-\frac{dc}{dt}\right)\times10^6$ mol dm^{-3} min^{-1}
2.50	36.58	36.28
1.66	34.00	34.22
1.25	30.53	30.86
1.00	30.12	30.00
0.66	26.62	26.26
0.50	24.48	24.88



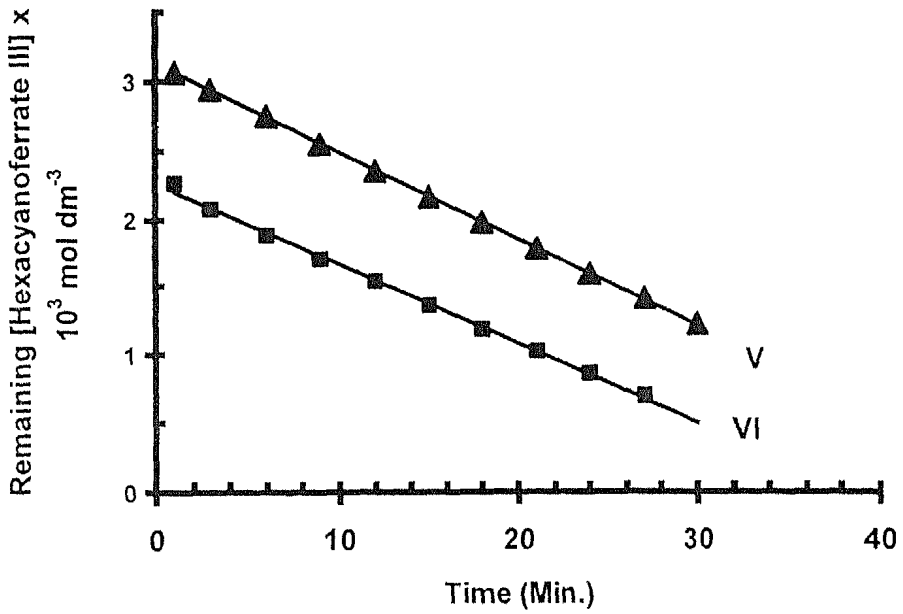


Figure 3.5 $[OH^-] = 1.00\times10^{-1}$ mol dm^{-3}; [Tetraethylene Glycol] = 2.50×10^{-2} mol dm^{-3}; [Ru(VI)]= 6.55×10^{-6} mol dm^{-3}, μ = 0.20 mol dm^{-3}.

	$[K_3Fe(CN)_6] \times 10^3$ mol dm^{-3}		
I	2.50	IV	1.00
II	1.66	V	0.66
III	1.25	VI	0.50

3.2 DETERMINATION OF THE ORDER OF THE REACTION WITH RESPECT TO RUTHENATE ION (Ru(VI)).

In order to determine the order of reaction with respect to ruthenate ion, experiments have been performed at varying concentration of ruthenate ion, i.e. Ru(VI), keeping the concentration of the other reactants and ionic strength constant. The concentration of ruthenate ion varied six to eight folds. In these runs also the velocity (-dc/dt) was determined from the zero order plot. Thus the value of (-dc/dt) obtained by graph and the values of k_s obtained by calculation are quite in agreement with each other.

4-methyl pentanol-2 has been taken as the first member to observe the effect of variation of ruthenate ion concentration on the reaction velocity. It has been found that the reaction velocity increases linearly with increase in ruthenate ion concentration. The results obtained are given in the tables (3.41 to 3.46). The table 3.47 represents the summarised results. When a graph is plotted between Ru(VI) Vs. rate i.e. (-dc/dt), a straight line passing through origin is obtained (Fig. 3.6(A)). This indicates that the reaction velocity has a linear dependence on ruthenate ion concentration. The effect of variation of ruthenate ion concentration has also been studied by changing the concentration of other reactants and results are summarised in the table (3.48). These results have also been reproduced in the form of graph (fig. 3.6(B)) and again confirms the linear dependence on ruthenate ion concentration.

Table 3.41

Temp. = 35°C

$[K_3Fe(CN)_6]$ = 2.00×10^{-3} mol dm^{-3}

$[OH^-]$ = 10×10^{-2} mol dm^{-3}

[4-methyl pentanol-2] = 4.00×10^{-2} mol dm^{-3}

[Ru(VI)] = 2.18×10^{-6} mol dm^{-3}

μ = 0.25 M

Time min	$Ce(SO_4)_2$ 1.25×10^{-3}M in ml.	$k_0\times10^2$ ml min^{-1}
1	0.84	
3	1.10	13.00
6	1.46	12.00
9	1.84	12.60
12	2.24	13.33
15	2.62	12.60
20	3.20	11.60
25	3.82	12.40
30	4.44	12.40
35	5.10	13.20
40	5.60	10.00*
T_∞	8.00	

Average $k_0 = 12.56\times10^{-2}$ ml min^{-1}

A.D. = ± 3.32%

$k_s = 31.40\times10^{-6}$ mol dm^{-3} min^{-1}

$\left(-\frac{dc}{dt}\right) = 31.45\times10^{-6}$ mole dm^{-3} min^{-1}

Table 3.42

Temp. = 35°C

$[K_3Fe(CN)_6]$ = 2.00×10^{-3} mol dm^{-3}

$[OH^-]$ = 10×10^{-2} mol dm^{-3}

[4-methyl pentanol-2] = 4.00×10^{-2} mol dm^{-3}

[Ru(VI)] = 2.61×10^{-6} mol dm^{-3}

μ = 0.25 M

Time min	$Ce(SO_4)_2$ 1.25×10^{-3}M in ml.	$k_0\times10^2$ ml min^{-1}
1	0.90	
3	1.20	15.00
6	1.66	15.30
9	2.12	15.30
12	2.60	16.00
15	3.10	16.60
18	3.56	15.30
21	4.00	14.60
24	4.46	15.30
27	4.90	14.60
30	5.40	16.60
35	5.90	10.00*
T_∞	8.00	

Average $k_0 = 15.36\times10^{-2}$ ml min^{-1}

A.D. = ± 3.41%

$k_s = 38.40\times10^{-6}$ mol dm^{-3} min^{-1}

$\left(-\frac{dc}{dt}\right) = 38.44\times10^{-6}$ mole dm^{-3} min^{-1}

Table 3.43

Temp. = 35°C

$[K_3Fe(CN)_6]$ = 2.00×10^{-3} mol dm^{-3}

$[OH^-]$ = 10×10^{-2} mol dm^{-3}

[4-methyl pentanol-2] = 4.00×10^{-2} mol dm^{-3}

[Ru(VI)] = 3.27×10^{-6} mol dm^{-3}

μ = 0.25 M

Time min	$Ce(SO_4)_2$ 1.25×10^{-3}M in ml.	$k_0\times10^2$ ml min^{-1}
1	0.94	
3	1.30	18.00
6	1.84	18.00
9	2.44	20.00
12	3.10	22.00
15	3.66	18.60
18	4.18	17.30
21	4.70	17.30
24	5.20	16.60
27	5.70	16.60
30	6.00	10.00*
T_∞	8.00	

Average $k_0 = 18.3\times10^{-2}$ ml min^{-1}

A.D. = ± 6.44%

$k_s = 45.75\times10^{-6}$ mol dm^{-3} min^{-1}

$\left(-\frac{dc}{dt}\right) = 45.80\times10^{-6}$ mole dm^{-3} min^{-1}

Table 3.44

Temp. =35°C

$[K_3Fe(CN)_6]$ = 2.00×10^{-3}mol dm^{-3}

$[OH^-]$ = 10×10^{-2} mol dm^{-3}

[4-methyl pentanol-2] = 4.00×10^{-2} mol dm^{-3}

[Ru(VI)] = 4.36×10^{-6} mol dm^{-3}

μ = 0.25 M

Time min	$Ce(SO_4)_2$ 1.25×10^{-3}M in ml.	$k_0\times10^2$ ml min^{-1}
1	0.96	
3	1.48	26.00
6	2.26	26.00
9	3.04	26.00
12	3.80	25.30
15	4.56	25.30
18	5.30	24.60
21	6.04	24.60
24	6.76	24.00
27	7.00	8.00*
T_∞	8.00	

Average $k_0 = 25.2\times10^{-2}$ ml min^{-1}

A.D. = ± 2.48%

$k_s = 63.0\times10^{-6}$ mol dm^{-3} min^{-1}

$\left(-\frac{dc}{dt}\right) = 62.96\times10^{-6}$ mole dm^{-3} min^{-1}

Table 3.45

Temp. = 35°C

$[K_3Fe(CN)_6]$ = 2.00×10^{-3} mol dm^{-3}

$[OH^-]$ = 10×10^{-2} mol dm^{-3}

[4-methyl pentanol-2] = 4.00×10^{-2} mol dm^{-3}

[Ru(VI)] = 5.45×10^{-6} mol dm^{-3}

μ = 0.25 M

Time min	$Ce(SO_4)_2$ 1.25×10^{-3}M in ml.	$k_0\times10^2$ ml min^{-1}
1	1.04	
3	1.68	32.00
5	2.32	32.00
7	2.94	31.00
9	3.58	32.00
11	4.20	31.00
13	4.82	31.00
15	5.46	32.00
17	6.06	30.00
19	6.56	25.00*
T_∞	8.00	

Average $k_0 = 31.30\times10^{-2}$ ml min^{-1}

A.D. = ± 1.99%

$k_s = 78.25\times10^{-6}$ mol dm^{-3} min^{-1}

$\left(-\frac{dc}{dt}\right) = 78.30\times10^{-6}$ mole dm^{-3} min^{-1}

Table 3.46

Temp. = 35°C

$[K_3Fe(CN)_6]$ = 2.00×10^{-3} mol dm^{-3}

$[OH^-]$ = 10×10^{-2} mol dm^{-3}

[4-methyl pentanol-2] = 4.00×10^{-2} mol dm^{-3}

[Ru(VI)] = 6.54×10^{-6} mol dm^{-3}

μ = 0.25 M

Time min	$Ce(SO_4)_2$ 1.25×10^{-3}M in ml.	$k_0\times10^2$ ml min^{-1}
1	1.14	
3	1.94	40.00
5	2.72	39.00
6	3.12	40.00
8	3.92	40.00
10	4.70	39.00
12	5.46	38.00
14	6.22	38.00
17	7.10	29.30*
T_∞	8.00	

Average $k_0 = 39.00\times10^{-2}$ ml min^{-1}

A.D. = ± 1.82%

$k_s = 97.50\times10^{-6}$ mol dm^{-3} min^{-1}

$\left(-\frac{dc}{dt}\right) = 97.00\times10^{-6}$ mole dm^{-3} min^{-1}

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Table 3.47

Temp. = 35°C
$[K_3Fe(CN)_6]$ = 2.00×10^{-3} mol dm^{-3}
$[OH^-]$ = 10×10^{-2} mol dm^{-3}
[4-methyl-pentanol] = 4.00×10^{-2} mol dm^{-3}
μ = 0.25 mol dm^{-3}

$[Ru(VI)]\times10^6$ mol dm^{-3}	$k_s\times10^6$ mol dm^{-3} min^{-1}	$\left(-\frac{dc}{dt}\right)\times10^6$ mol dm^{-3} min^{-1}	$\frac{k_s}{[Ru(VI)]}$ min^{-1}
6.54	97.50	97.00	14.90
5.45	78.25	78.30	14.35
4.36	63.00	62.96	14.44
3.27	45.75	45.80	13.99
2.61	38.40	38.44	14.70
2.18	31.40	31.45	14.40

Table 3.48

Temp. = 35°C
$[K_3Fe(CN)_6]$ = 2.00×10^{-3} mol dm^{-3}
$[OH^-]$ = 10×10^{-2} mol dm^{-3}
[4-methyl-pentanol-2] = 2.00×10^{-2} mol dm^{-3}
μ = 0.25 mol dm^{-3}

$[Ru(VI)]\times10^6$ mol dm^{-3}	$k_s\times10^6$ mol dm^{-3} min^{-1}	$\left(-\frac{dc}{dt}\right)\times10^6$ mol dm^{-3} min^{-1}	$\frac{k_s}{[Ru(VI)]}$ min^{-1}
6.54	53.62	54.00	8.19
5.45	41.80	42.02	7.66
4.36	34.40	34.18	7.88
3.27	28.44	28.42	8.69
2.18	18.13	18.64	8.31
1.09	7.81	7.96	7.16

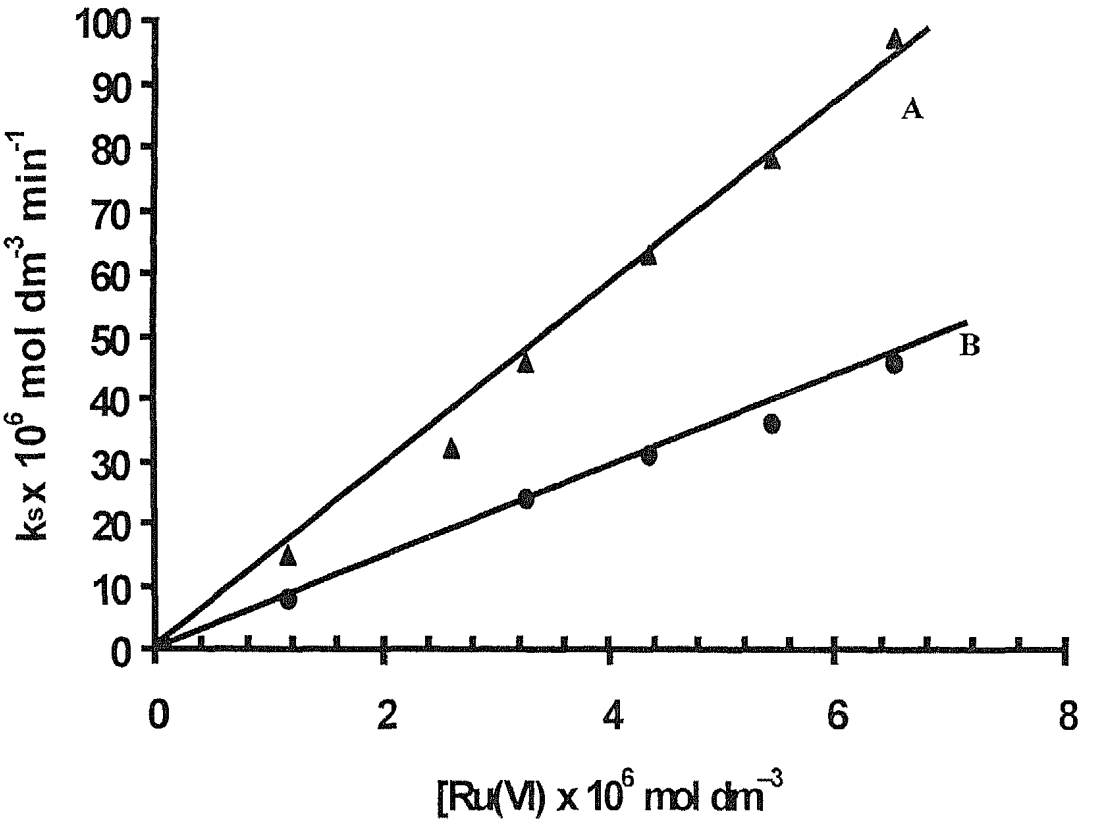


Figure 3.6

Temp. = 35°C; $[K_3Fe(CN)_6]$= 2.00 × 10^{-3} mol dm^{-3}; $[OH^-]$= 10×10^{-2} mol dm^{-3}; [4-Methyl Pentanol-2]= (A) 4.00×10^{-2} mol dm^{-3} (B)= 2.00×10^{-2} mol dm^{-3}; μ = 0.25 mol dm^{-3}

2-methoxy ethanol was taken as second compound to study the effect of variation of concentration of ruthenate ion on the reaction velocity. The results obtained at different concentrations of ruthenate ion are given in the tables (3.49 to 3.54). The summarised results are given in the table (3.55 and 3.56). A close observation of tables (3.49 to 3.54) indicates that the order with respect to ruthenate ion is unity because the reaction velocity increases linearly with increase in ruthenate ion concentration. When a graph is plotted between [Ru(VI)] Vs. rate, a straight line passing through origin, is obtained (Fig.3.7(A) and 3.7(B)). This further confirms that the order of reaction with respect to ruthenate ion is unity.

Table 3.49

Temp. = 35°C

$[K_3Fe(CN)_6]$ = 2.00×10^{-3} mol dm^{-3}

$[OH^-]$ = 10×10^{-2} mol dm^{-3}

[2-Methoxy Ethanol] = 5.00×10^{-2} mol dm^{-3}

[Ru(VI)] = 7.75×10^{-7} mol dm^{-3}

μ = 0.20 mol dm^{-3}

Time min	$Ce(SO_4)_2$ 1.00×10^{-3}M in ml.	$k_0\times10^2$ ml min^{-1}
1	0.76	
5	1.16	10.00
10	1.68	10.40
15	2.20	10.40
20	2.70	10.00
25	3.18	9.60
30	3.66	9.60
35	4.14	9.60
40	4.60	9.20
45	5.08	9.60
50	5.54	9.20
T∞	10.00	

Average $k_0 = 9.76\times10^{-2}$ ml min^{-1}

A.D. = ± 3.60%

$k_s = 19.52\times10^{-6}$ mol dm^{-3} min^{-1}

$\left(-\frac{dc}{dt}\right) = 19.60\times10^{-6}$ mole dm^{-3} min^{-1}

Table 3.50

Temp. = 35°C

$[K_3Fe(CN)_6]$ = 2.00×10^{-3} mol dm^{-3}

$[OH^-]$ = 10×10^{-2} mol dm^{-3}

[2-Methoxy Ethanol] = 5.00×10^{-2} mol dm^{-3}

[Ru(VI)] = 15.5×10^{-7} mol dm^{-3}

μ = 0.20 mol dm^{-3}

Time min	$Ce(SO_4)_2$ 1.00×10^{-3}M in ml.	$k_0\times10^2$ ml min^{-1}
1	0.80	
3	1.20	20.00
6	1.82	20.60
9	2.44	20.60
12	3.04	20.00
15	3.64	20.00
18	4.24	20.00
21	4.82	19.30
24	5.40	19.30
27	5.98	19.30
30	6.56	19.30
T∞	10.00	

Average $k_0 = 19.80\times10^{-2}$ ml min^{-1}

A.D. = ± 2.22%

$k_s = 39.60\times10^{-6}$ mol dm^{-3} min^{-1}

$\left(-\frac{dc}{dt}\right) = 40.00\times10^{-6}$ mole dm^{-3} min^{-1}

Table 3.51

Temp. = 35°C

$[K_3Fe(CN)_6]$ = 2.00×10^{-3} mol dm^{-3}

$[OH^-]$ = 10×10^{-2} mol dm^{-3}

[2-Methoxy Ethanol] = 5.00×10^{-2} mol dm^{-3}

[Ru(VI)] = 23.25×10^{-7} mol dm^{-3}

μ = 0.20 mol dm^{-3}

Time min	$Ce(SO_4)_2$ 1.00×10^{-3}M in ml.	$k_0\times10^2$ ml min^{-1}
1	0.86	
3	1.46	30.00
5	2.06	30.00
7	2.64	29.00
9	3.24	30.00
11	3.82	29.00
13	4.40	29.00
15	4.98	29.00
17	5.56	29.00
19	6.12	28.00
21	6.68	28.00
23	7.04	18.00*
T_∞	10.00	

Average $k_0 = 29.10\times10^{-2}$ ml min^{-1}

A.D. = ± 1.85%

$k_s = 58.20\times10^{-6}$ mol dm^{-3} min^{-1}

$\left(-\frac{dc}{dt}\right) = 58.60\times10^{-6}$ mole dm^{-3} min^{-1}

Table 3.52

Temp. = 35°C

$[K_3Fe(CN)_6]$ = 2.00×10^{-3} mol dm^{-3}

$[OH^-]$ = 10×10^{-2} mol dm^{-3}

[2-Methoxy Ethanol] = 5.00×10^{-2} mol dm^{-3}

[Ru(VI)] = 31.0×10^{-7} mol dm^{-3}

μ = 0.20 mol dm^{-3}

Time min	$Ce(SO_4)_2$ 1.00×10^{-3}M in ml.	$k_0\times10^2$ ml min^{-1}
1	0.90	
3	1.70	40.00
5	2.48	39.00
7	3.26	39.00
9	4.06	40.00
11	4.84	39.00
13	5.62	39.00
15	6.40	39.00
17	7.06	33.00*
T_∞	10.00	

Average $k_0 = 38.90\times10^{-2}$ ml min^{-1}

A.D. = ± 0.98%

$k_s = 77.80\times10^{-6}$ mol dm^{-3} min^{-1}

$\left(-\frac{dc}{dt}\right) = 77.50\times10^{-6}$ mole dm^{-3} min^{-1}

Table 3.53

Temp. = 35°C
$[K_3Fe(CN)_6]$ = 2.00×10^{-3} mol dm^{-3}
$[OH^-]$ = 10×10^{-2} mol dm^{-3}
[2-Methoxy Ethanol] = 5.00×10^{-2} mol dm^{-3}
[Ru(VI)] = 38.75×10^{-7} mol dm^{-3}
μ = 0.20 mol dm^{-3}

Time min	$Ce(SO_4)_2$ 1.00×10^{-3}M in ml.	$k_0\times10^2$ ml min^{-1}
1	0.92	
2	1.42	50.00
3	1.92	50.00
4	2.40	48.00
5	2.88	48.00
6	3.38	50.00
7	3.86	48.00
8	4.36	50.00
9	4.86	50.00
10	5.36	50.00
11	5.84	48.00
T_∞	10.00*	

Average $k_0 = 49.2\times10^{-2}$ ml min^{-1}
A.D. = ± 1.95%
$k_s = 98.4\times10^{-6}$ mol dm^{-3} min^{-1}
$\left(-\frac{dc}{dt}\right) = 98.0\times10^{-6}$ mole dm^{-3} min^{-1}

Table 3.54

Temp. = 35°C
$[K_3Fe(CN)_6]$ = 2.00×10^{-3} mol dm^{-3}
$[OH^-]$ = 10×10^{-2} mol dm^{-3}
[2-Methoxy Ethanol] = 5.00×10^{-2} mol dm^{-3}
[Ru(VI)] = 46.50×10^{-7} mol dm^{-3}
μ = 0.20 mol dm^{-3}

Time min	$Ce(SO_4)_2$ 1.00×10^{-3}M in ml.	$k_0\times10^2$ ml min^{-1}
1	0.98	
2	1.58	60.00
3	2.18	60.00
4	2.76	58.00
5	3.34	58.00
6	3.94	60.00
7	4.52	58.00
8	5.08	56.00
9	5.64	56.00
10	6.22	58.00
11	6.78	56.00
T∞	10.00	

Average $k_0 = 58.00\times10^{-2}$ ml min^{-1}
A.D. = ± 2.06%
$k_s = 116.0\times10^{-6}$ mol dm^{-3} min^{-1}
$\left(-\frac{dc}{dt}\right) = 115.8\times10^{-6}$ mole dm^{-3} min^{-1}

Table 3.55

Temp. = 35°C
$[K_3Fe(CN)_6]$ = 2.00×10^{-3} mol dm^{-3}
$[OH^-]$ = 10×10^{-2} mol dm^{-3}
[2-Methoxy Ethanol] = 5.00×10^{-2} mol dm^{-3}
μ = 0.20 mol dm^{-3}

$[Ru(VI)]\times10^7$ mol dm^{-3}	$k_s\times10^6$ mol dm^{-3} min^{-1}	$\left(-\frac{dc}{dt}\right)\times10^6$ mol dm^{-3} min^{-1}	$\frac{k_s}{[Ru(VI)]}\times10^{-1}$ min^{-1}
7.75	19.52	19.60	2.51
15.50	39.60	40.00	2.55
23.25	58.20	58.60	2.50
31.00	77.80	77.50	2.50
38.75	98.40	98.00	2.53
46.50	116.00	115.80	2.49

Table 3.56

Temp. = 35°C
$[K_3Fe(CN)_6]$ = 2.00×10^{-3} mol dm^{-3}
$[OH^-]$ = 10×10^{-2} mol dm^{-3}
[2-Methoxy Ethanol] = 2.50×10^{-2} mol dm^{-3}
μ = 0.20 mol dm^{-3}

$[Ru(VI)]\times10^7$ mol dm^{-3}	$k_s\times10^6$ mol dm^{-3} min^{-1}	$\left(-\frac{dc}{dt}\right)\times10^6$ mol dm^{-3} min^{-1}	$\frac{k_s}{[Ru(VI)]}\times10^{-1}$ min^{-1}
7.75	10.40	10.98	1.34
15.50	21.40	21.36	1.38
23.25	32.90	32.82	1.41
31.00	42.20	42.88	1.36
38.75	53.00	53.65	1.36
46.50	63.60	63.86	1.36

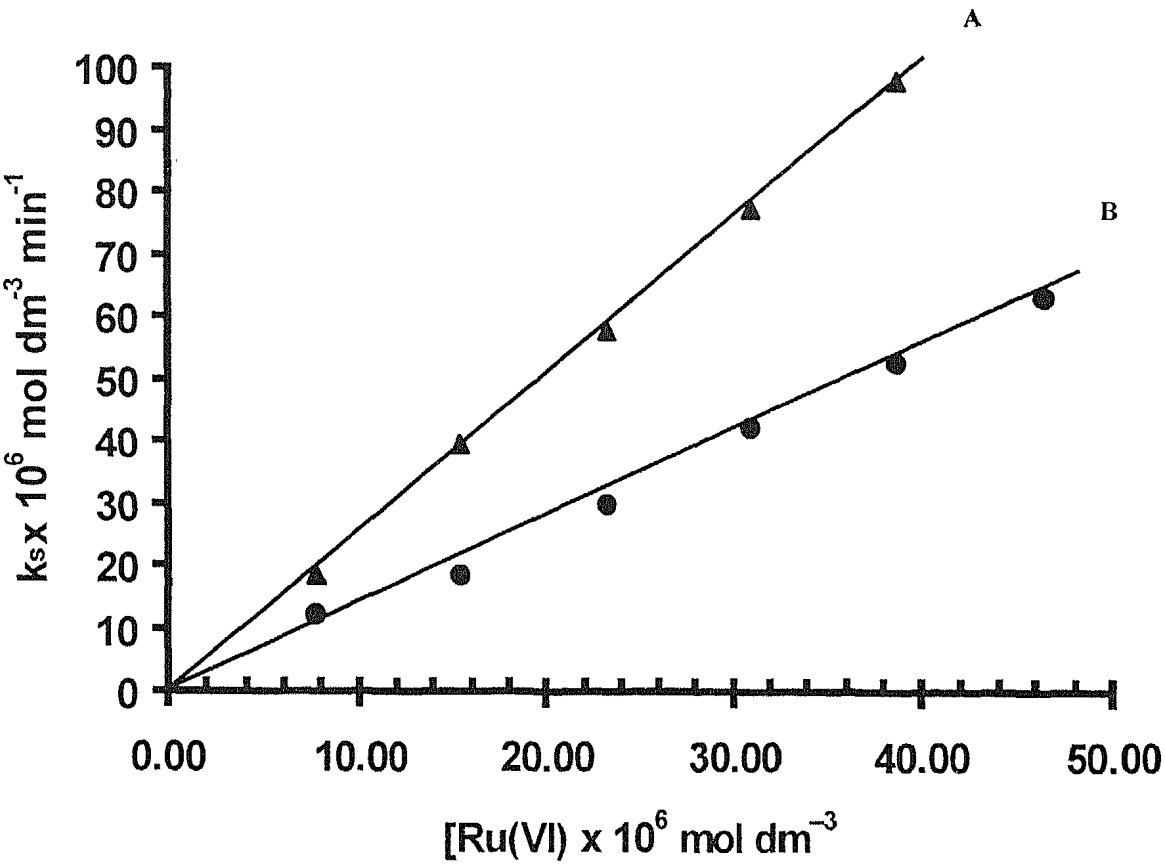


Figure 3.7

Temp. = 35°C; $[K_3Fe(CN)_6] = 2.00 \times 10^{-3}$ mol dm^{-3}; $[OH^-] = 10 \times 10^{-2}$ mol dm^{-3}; [2-Methoxy Ethanol]= (A) 5.00×10^{-2} mol dm^{-3}, (B) 2.50×10^{-2} mol dm^{-3}; $\mu = 0.20$ mol dm^{-3}

Diethylene glycol was taken as third compound to study the effect of variation of concentration of ruthenate ion on the reaction velocity. The results obtained at different concentrations of ruthenate ion are given in the tables (3.57 to 3.62). The summarised results are given in the table (3.63 and 3.64). A close observation of tables (3.57 to 3.62) clearly indicates that the order with respect to ruthenate ion is unity since the reaction velocity increases linearly with increase in ruthenate ion concentration. When a graph is plotted between [Ru(VI)] Vs. rate, a straight line passing through origin, is obtained (Fig.3.8(A) and 3.8(B)). This further confirms that the order of reaction with respect to ruthenate ion is unity.

Table 3.57

Temp. = 30°C

$[K_3Fe(CN)_6]$ = 2.00×10^{-3} mol dm^{-3}

$[OH^-]$ = $10\ 0\times10^{-2}$ mol dm^{-3}

[Diethylene glycol] = 3.125×10^{-2} mol dm^{-3}

[Ru(VI)] = $1\ 82\times10^{-6}$ mol dm^{-3}

μ = 0.25 mol dm^{-3}

Time min	$Ce(SO_4)_2$ 1.00×10^{-3}M in ml.	$k_0\times10^2$ ml min^{-1}
1	0.36	
5	0.56	5.00
10	0.80	4.80
15	1.06	5.20
20	1.32	5.20
25	1.56	4.80
30	1.80	4.80
35	2.02	4.40
40	2.24	4.40
45	2.48	4.80
50	2.72	4.80
I∞	10.00	

Average $k_0 = 4.82\times10^{-2}$ ml min^{-1}

A.D. = ± 3.90%

$k_s = 9.64\times10^{-6}$ mol dm^{-3} min^{-1}

$\left(-\frac{dc}{dt}\right) = 9.70\times10^{-6}$ mole dm^{-3} min^{-1}

Table 3.58

Temp. = 30°C

$[K_3Fe(CN)_6]$ = 2.00×10^{-3} mol dm^{-3}

$[OH^-]$ = 10.0×10^{-2} mol dm^{-3}

[Diethylene glycol] = 3.125×10^{-2} mol dm^{-3}

[Ru(VI)] = 3.66×10^{-6} mol dm^{-3}

μ = 0.25 mol dm^{-3}

Time min	$Ce(SO_4)_2$ 1.00×10^{-3}M in ml.	$k_0\times10^2$ ml min^{-1}
1	0.38	
5	0.78	10.00
10	1.26	9.60
15	1.74	9.60
20	2.20	9.20
25	2.66	9.20
30	3.12	9.20
35	3.58	9.20
40	4.02	8.80
45	4.46	8.80
50	4.90	8.80
T∞	10.00	

Average $k_0 = 9.24\times10^{-2}$ ml min^{-1}

A.D. = ± 3.20%

$k_s = 18.48\times10^{-6}$ mol dm^{-3} min^{-1}

$\left(-\frac{dc}{dt}\right) = 18.50\times10^{-6}$ mole dm^{-3} min^{-1}

Table 3.59

Temp. = 30°C
$[K_3Fe(CN)_6]$ = 2.00×10^{-3} mol dm^{-3}
$[OH^-]$ = 10.0×10^{-2} mol dm^{-3}
[Diethylene glycol] = 3.12×10^{-2} mol dm^{-3}
[Ru(VI)] = 5.47×10^{-6} mol dm^{-3}
μ = 0.25 mol dm^{-3}

Time min	$Ce(SO_4)_2$ 1.00×10^{-3}M in ml.	$k_0\times10^2$ ml min^{-1}
1	0.40	
5	0.96	14.00
10	1.64	13.60
15	2.34	14.00
20	3.02	13.60
25	3.70	13.60
30	4.36	13.60
35	5.02	13.20
40	5.68	13.20
45	6.34	13.20
50	7.00	13.20
T∞	10.00	

Average $k_0 = 13.52\times10^{-2}$ ml min^{-1}
A.D. = ± 1.89%
$k_s = 27.4\times10^{-6}$ mol dm^{-3} min^{-1}
$\left(-\frac{dc}{dt}\right) = 27.0\times10^{-6}$ mole dm^{-3} min^{-1}

Table 3.60

Temp. = 30°C
$[K_3Fe(CN)_6]$ = 2.00×10^{-3} mol dm^{-3}
$[OH^-]$ = 10.0×10^{-2} mol dm^{-3}
[Diethylene glycol] = 3.12×10^{-2} mol dm^{-3}
[Ru(VI)] = 7.33×10^{-6} mol dm^{-3}
μ = 0.25 mol dm^{-3}

Time min	$Ce(SO_4)_2$ 1.00×10^{-3}M in ml.	$k_0\times10^2$ ml min^{-1}
1	0.44	
3	1.02	19.30
6	1.58	18.60
9	2.14	18.60
12	2.68	18.00
15	3.22	18.00
18	3.74	17.30
21	4.26	17.30
24	4.78	17.30
27	5.30	17.30
30	5.80	16.60
T∞	10.00	

Average $k_0 = 17.83\times10^{-2}$ ml min^{-1}
A.D. = ± 3.53%
$k_s = 35.66\times10^{-6}$ mol dm^{-3} min^{-1}
$\left(-\frac{dc}{dt}\right) = 35.70\times10^{-6}$ mole dm^{-3} min^{-1}

Table 3.61

Temp. = 30°C

$[K_3Fe(CN)_6]$ = 2.00×10^{-3} mol dm^{-3}

$[OH^-]$ = 10.0×10^{-2} mol dm^{-3}

[Diethylene glycol] = 3.12×10^{-2} mol dm^{-3}

[Ru(VI)] = 9.12×10^{-6} mol dm^{-3}

μ = 0.25 mol dm^{-3}

Time min	$Ce(SO_4)_2$ 1.00×10^{-3}M in ml.	$k_0\times10^2$ ml min^{-1}
1	0.44	
3	0.92	24.00
6	1.62	23.30
9	2.34	24.00
12	3.04	23.30
15	3.74	23.30
18	4.42	22.60
21	5.10	22.60
24	5.80	23.30
27	6.48	22.60
30	7.14	22.00
T_∞	10.00	

Average $k_0 = 23.10\times10^{-2}$ ml min^{-1}

A.D. = ± 2.25%

$k_s = 46.20\times10^{-6}$ mol dm^{-3} min^{-1}

$\left(-\frac{dc}{dt}\right) = 45.70\times10^{-6}$ mole dm^{-3} min^{-1}

Table 3.62

Temp. = 30°C

$[K_3Fe(CN)_6]$ = 2.00×10^{-3} mol dm^{-3}

$[OH^-]$ = 10.0×10^{-2} mol dm^{-3}

[Diethylene glycol] = 3.12×10^{-2} mol dm^{-3}

[Ru(VI)] = 10.95×10^{-6} mol dm^{-3}

μ = 0.25 mol dm^{-3}

Time min	$Ce(SO_4)_2$ 1.00×10^{-3}M in ml.	$k_0\times10^2$ ml min^{-1}
1	0.46	
3	1.02	28.00
5	1.58	28.00
7	2.12	27.00
9	2.66	27.00
11	3.18	26.00
13	3.60	26.00
15	4.12	26.00
17	4.66	27.00
19	5.20	27.00
21	5.74	27.00
T∞	10.00	

Average $k_0 = 26.9\times10^{-2}$ ml min^{-1}

A.D. = ± 2.00%

$k_s = 53.80\times10^{-6}$ mol dm^{-3} min^{-1}

$\left(-\frac{dc}{dt}\right) = 54.0\times10^{-6}$ mole dm^{-3} min^{-1}

Table 3.63

Temp. = 30°C
$[K_3Fe(CN)_6]$ = 2.00×10^{-3} mol dm^{-3}
$[OH^-]$ = 1.00×10^{-1} mol dm^{-3}
[Diethylene glycol] = 3.125×10^{-2} mol dm^{-3}
μ = 0.25 mol dm^{-3}

$[Ru(VI)]\times10^6$ mol dm^{-3}	$k_s\times10^6$ mol dm^{-3} min^{-1}	$\left(-\frac{dc}{dt}\right)\times10^6$ mol dm^{-3} min^{-1}	$\frac{k_s}{[Ru(VI)]}$ min^{-1}
1.82	9.64	9.70	5.29
3.66	18.48	18.50	5.04
5.47	27.40	27.00	5.00
7.33	35.66	35.70	4.86
9.12	46.20	45.70	5.06
10.95	53.80	54.00	4.91

Table 3.64

Temp. = 30°C
$[K_3Fe(CN)_6]$ = 2.00×10^{-3} mol dm^{-3}
$[OH^-]$ = 10×10^{-2} mol dm^{-3}
[Diethylene glycol] = 2.00×10^{-2} mol dm^{-3}
μ = 0.25 mol dm^{-3}

$[Ru(VI)]\times10^6$ mol dm^{-3}	$k_s\times10^6$ mol dm^{-3} min^{-1}	$\left(-\frac{dc}{dt}\right)\times10^6$ mol dm^{-3} min^{-1}	$\frac{k_s}{[Ru(VI)]}$ min^{-1}
1.82	6.50	6.66	3.57
3.66	13.90	13.65	3.77
5.47	19.06	20.00	3.48
7.33	25.25	26.20	3.44
9.12	32.34	32.86	3.54
10.95	38.65	39.12	3.52

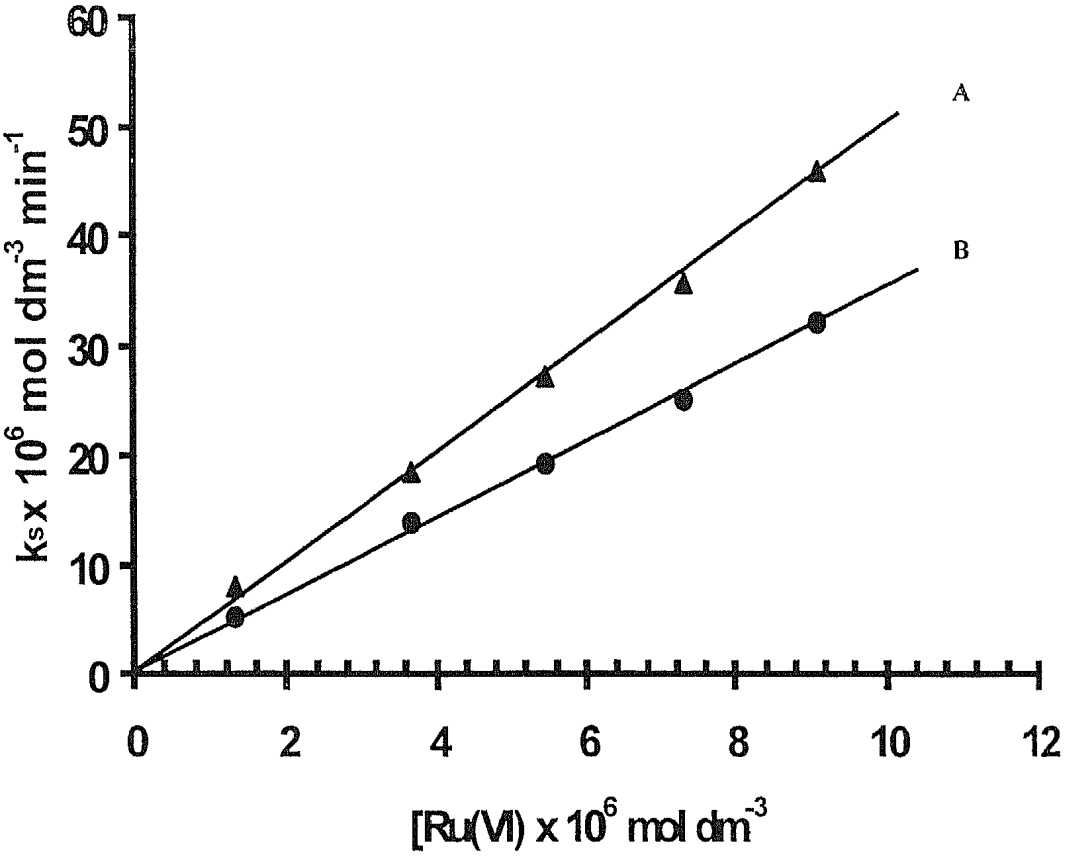


Figure 3.8

Temp. = 30°C; $[K_3Fe(CN)_6] = 2.00 \times 10^{-3}$ mol dm^{-3}; $[OH^-] = 10 \times 10^{-2}$ mol dm^{-3}; [Diethylene Glycol]= (A) 3.125×10^{-2} mol dm^{-3}, (B) 2.0×10^{-2} mol dm^{-3}; $\mu = 0.25$ mol dm^{-3}

Triethlene glycol was taken as the fourth compound to study the kinetic effect of variation of concentration of ruthenate ion on the reaction velocity. The results obtained at different concentrations of ruthenate ion are given in the tables (3.65 to 3.70). The summarised results are given in the table (3.71 and 3.72). A close observation of tables (3.65 to 3.70) indicates that the order with respect to ruthenate ion is unity since the reaction velocity increases linearly with increase in ruthenate ion concentration. When a graph is plotted between [Ru(VI)] Vs. rate, a straight line passing through origin, is obtained (Fig.3.9(A) and 3.9(B)). This further confirms that the order of reaction with respect to ruthenate ion Ru(IV) is unity.

Table 3.65

Temp. = 35°C
$[K_3Fe(CN)_6]$ = 2.00×10^{-3} mol dm^{-3}
$[OH^-]$ = 10.0×10^{-2} mol dm^{-3}
[Triethylene glycol] = 5.00×10^{-2} mol dm^{-3}
[Ru(VI)] = 1.2×10^{-6} mol dm^{-3}
μ = 0.20 mol dm^{-3}

Time min	$Ce(SO_4)_2$ 1.00×10^{-3}M in ml.	$k_0\times10^2$ ml min^{-1}
1	0.60	
5	0.92	8.00
10	1.30	7.60
15	1.68	7.60
20	2.08	8.00
25	2.46	7.60
30	2.84	7.60
35	3.20	7.20
40	3.56	7.20
45	3.92	7.20
50	4.28	7.20
T∞	10.00	

Average $k_0 = 7.52\times10^{-2}$ mol min^{-1}
A.D. = ± 3.40%
$k_s = 15.05\times10^{-6}$ mol dm^{-3} min^{-1}
$\left(-\frac{dc}{dt}\right) = 15.00\times10^{-6}$ mole dm^{-3} min^{-1}

Table 3.66

Temp. = 35°C
$[K_3Fe(CN)_6]$ = 2.00×10^{-3} mol dm^{-3}
$[OH^-]$ = 10.0×10^{-2} mol dm^{-3}
[Triethylene glycol] = 5.00×10^{-2} mol dm^{-3}
[Ru(VI)] = 2.41×10^{-6} mol dm^{-3}
μ = 0.20 mol dm^{-3}

Time min	$Ce(SO_4)_2$ 1.00×10^{-3}M in ml.	$k_0\times10^2$ ml min^{-1}
1	0.64	
5	1.18	13.50
10	1.86	13.60
15	2.52	13.20
20	3.18	13.20
25	3.82	12.80
30	4.46	12.80
35	5.10	12.80
40	5.74	12.80
45	6.40	13.20
50	7.02	12.40
T∞	10.00	

Average $k_0 = 13.03\times10^{-2}$ ml min^{-1}
A.D. = ± 2.37%
$k_s = 26.06\times10^{-6}$ mol dm^{-3} min^{-1}
$\left(-\frac{dc}{dt}\right) = 26.10\times10^{-6}$ mole dm^{-3} min^{-1}

Table 3.67

Temp. = 35°C
$[K_3Fe(CN)_6]$ = 2.00×10^{-3} mol dm^{-3}
$[OH^-]$ = 10.0×10^{-2} mol dm^{-3}
[Triethylene glycol] = 5.00×10^{-2} mol dm^{-3}
[Ru(VI)] = 3.60×10^{-6} mol dm^{-3}
μ = 0.20 mol dm^{-3}

Time min	$Ce(SO_4)_2$ 1.00×10^{-3}M in ml.	$k_0\times10^2$ ml min^{-1}
1	0.72	
3	1.08	18.00
6	1.64	18.60
9	2.20	18.60
12	2.74	18.00
15	3.28	18.00
18	3.82	18.00
21	4.34	17.30
24	4.88	18.00
27	5.40	17.30
30	5.92	17.30
T_∞	10.00	

Average $k_0 = 17.91\times10^{-2}$ ml min^{-1}
A.D. = ± 2.04%
$k_s = 35.82\times10^{-6}$ mol dm^{-3} min^{-1}
$\left(-\frac{dc}{dt}\right) = 35.86\times10^{-6}$ mole dm^{-3} min^{-1}

Table 3.68

Temp. = 35°C
$[K_3Fe(CN)_6]$ = 2.00×10^{-3} mol dm^{-3}
$[OH^-]$ = 10.0×10^{-2} mol dm^{-3}
[Triethylene glycol] = 5.00×10^{-2} mol dm^{-3}
[Ru(VI)] = 4.80×10^{-6} mol dm^{-3}
μ = 0.20 mol dm^{-3}

Time min	$Ce(SO_4)_2$ 1.00×10^{-3}M in ml.	$k_0\times10^2$ ml min^{-1}
1	0.80	
3	1.28	24.00
6	1.98	23.30
9	2.66	22.60
12	3.36	23.30
15	4.06	23.30
18	4.74	22.60
21	5.44	23.30
24	6.14	23.30
27	6.84	23.30
30	7.44	20.00*
T_∞	10.00	

Average $k_0 = 23.20\times10^{-2}$ ml min^{-1}
A.D. = ± 1.20%
$k_s = 47.20\times10^{-6}$ mol dm^{-3} min^{-1}
$\left(-\frac{dc}{dt}\right) = 47.25\times10^{-6}$ mole dm^{-3} min^{-1}

Table 3.69

Temp. = 35°C
$[K_3Fe(CN)_6]$ = 2.00×10^{-3} mol dm^{-3}
$[OH^-]$ = 10.0×10^{-2} mol dm^{-3}
[Triethylene glycol] = 5.00×10^{-2} mol dm^{-3}
[Ru(VI)] = 6.00×10^{-6} mol dm^{-3}
μ = 0.20 mol dm^{-3}

Time min	$Ce(SO_4)_2$ 1.00×10^{-3}M in ml.	$k_0\times10^2$ ml min^{-1}
1	0.88	
3	1.46	29.00
5	2.02	28.00
7	2.60	29.00
9	3.16	28.00
11	3.72	28.00
13	4.26	27.00
15	4.82	28.00
17	5.36	28.00
19	5.90	28.00
21	6.44	27.00
T_∞	10.00	

Average $k_0 = 28.00\times10^{-2}$ ml min^{-1}
A.D. = ± 1.42%
$k_s = 56.00\times10^{-6}$ mol dm^{-3} min^{-1}
$\left(-\frac{dc}{dt}\right) = 56.06\times10^{-6}$ mole dm^{-3} min^{-1}

Table 3.70

Temp. = 35°C
$[K_3Fe(CN)_6]$ = 2.00×10^{-3} mol dm^{-3}
$[OH^-]$ = 10.0×10^{-2} mol dm^{-3}
[Triethylene glycol] = 5.00×10^{-2} mol dm^{-3}
[Ru(VI)] = 7.20×10^{-6} mol dm^{-3}
μ = 0.20 mol dm^{-3}

Time min	$Ce(SO_4)_2$ 1.00×10^{-3}M in ml.	$k_0\times10^2$ ml min^{-1}
1	0.92	
2	1.26	34.00
4	1.94	34.00
6	2.60	33.00
8	3.28	34.00
10	3.98	35.00
12	4.64	33.00
14	5.32	34.00
16	6.02	35.00
18	6.70	34.00
20	7.20	25.00*
T∞	10.00	

Average $k_0 = 34.00\times10^{-2}$ ml min^{-1}
A.D. = ± 1.29%
$k_s = 68.00\times10^{-6}$ mol dm^{-3} min^{-1}
$\left(-\frac{dc}{dt}\right) = 68.05\times10^{-6}$ mole dm^{-3} min^{-1}

Table 3.71

Temp. = 35°C

$[K_3Fe(CN)_6]$ = 2.00×10^{-3} mol dm^{-3}

$[OH^-]$ = 10.00×10^{-2} mol dm^{-3}

[Triethylene glycol] = 5.00×10^{-2} mol dm^{-3}

μ = 0.20 mol dm^{-3}

$[Ru(VI)]\times10^6$ mol dm^{-3}	$k_s\times10^6$ mol dm^{-3} min^{-1}	$\frac{k_s}{[Ru(VI)]}$ min^{-1}
1.2	15.04	12.53
2.4	26.06	10.85
3.6	35.82	9.95
4.8	47.20	9.83
6.0	56.00	9.33
7.2	68.00	9.44

Table 3.72

Temp. = 35°C

$[K_3Fe(CN)_6]$ = 2.00×10^{-3} mol dm^{-3}

$[OH^-]$ = 10.00×10^{-2} mol dm^{-3}

[Triethylene glycol] = 2.50×10^{-2} mol dm^{-3}

μ = 0.20 mol dm^{-3}

$[Ru(VI)]\times10^6$ mol dm^{-3}	$k_s\times10^6$ mol dm^{-3} min^{-1}	$\frac{k_s}{[Ru(VI)]}$ min^{-1}
1.2	9.30	7.75
2.4	15.10	6.29
3.6	20.20	5.61
4.8	26.54	5.52
6.0	33.40	5.56
7.2	38.60	5.36

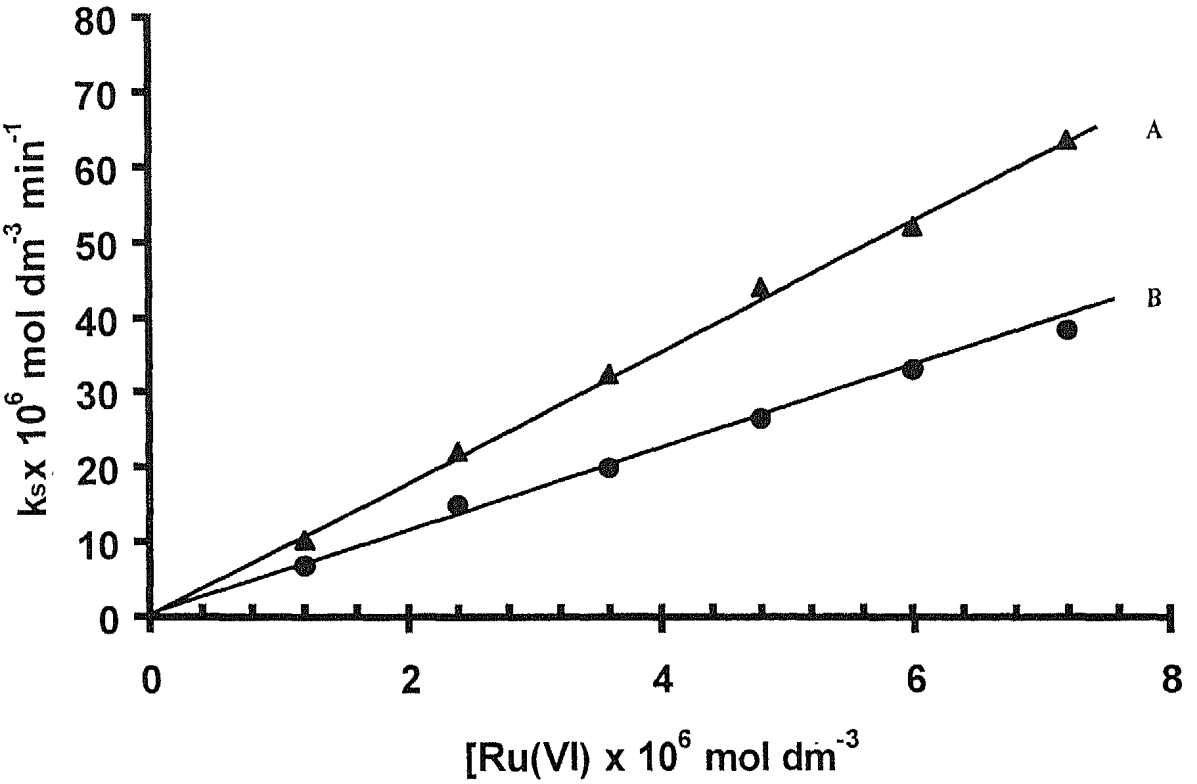


Figure 3.9 Temp. = 35°C; $[K_3Fe(CN)_6] = 2.00 \times 10^{-3}$ mol dm^{-3}; $[OH^-] = 10 \times 10^{-2}$ mol dm^{-3}; [Triethylene Glycol]= (A) 5.00×10^{-2} mol dm^{-3}, (B) 2.5×10^{-2} mol dm^{-3}; $\mu = 0.20$ mol dm^{-3}

Tetraethylene glycol was taken as the fifth compound to study the kinetic effect of variation of concentration of ruthenate ion on the reaction velocity. The results obtained at different concentrations of ruthenate ion are given in the tables (3.73 to 3.78). The summarised results are given in the table (3.79 and 3.80). A close observation of tables (3.73 to 3.78) indicates that the order with respect to ruthenate ion is unity. The reaction velocity increases linearly with increase in ruthenate ion concentration table 3.80. When a graph is plotted between [Ru(VI)] Vs. rate, a straight line passing through origin, is obtained (Fig.3.10(A) and 3.10(B)). This further confirms that the order of reaction with respect to ruthenate ion Ru(VI) is unity.

Table 3.73

Temp. = 35°C

$[K_3Fe(CN)_6]$ = 2.00×10^{-3} mol dm^{-3}

$[OH^-]$ = 10.0×10^{-2} mol dm^{-3}

[Tetraethylene glycol]= 2.00×10^{-2} mol dm^{-3}

[Ru(VI)] = 3.27×10^{-6} mol dm^{-3}

μ = 0.20 mol dm^{-3}

Time min	$Ce(SO_4)_2$ 1.00×10^{-3}M in ml.	$k_0\times10^2$ ml min^{-1}
1	0.30	
5	0.48	4.50
10	0.70	4.40
20	1.16	4.60
30	1.60	4.40
40	2.02	4.20
50	2.44	4.20
60	2.84	4.00
70	3.24	4.00
80	3.64	4.00
90	4.04	4.00
T∞	10.00	

Average $k_0 = 4.27\times10^{-2}$ ml min^{-1}

A.D. = ± 4.77%

$k_s = 8.54\times10^{-6}$ mol dm^{-3} min^{-1}

$\left(-\frac{dc}{dt}\right) = 8.56\times10^{-6}$ mole dm^{-3} min^{-1}

Table 3.74

Temp. = 35°C

$[K_3Fe(CN)_6]$ = 2.00×10^{-3} mol dm^{-3}

$[OH^-]$ = 10.0×10^{-2} mol dm^{-3}

[Tetraethylene glycol]= 2.00×10^{-2} mol dm^{-3}

[Ru(VI)] = 6.55×10^{-6} mol dm^{-3}

μ = 0.20 mol dm^{-3}

Time min	$Ce(SO_4)_2$ 1.00×10^{-3}M in ml.	$k_0\times10^2$ ml min^{-1}
1	0.38	
5	0.74	9.00
10	1.20	9.20
15	1.68	9.60
20	2.14	9.20
25	2.60	9.20
30	3.06	9.20
35	3.50	8.80
40	3.96	9.20
45	4.40	8.80
50	4.84	8.80
T∞	10.00	

Average $k_0 = 9.10\times10^{-2}$ ml min^{-1}

A.D. = ± 2.19%

$k_s = 18.20\times10^{-6}$ mol dm^{-3} min^{-1}

$\left(-\frac{dc}{dt}\right) = 18.26\times10^{-6}$ mole dm^{-3} min^{-1}

Table 3.75

Temp. = 35°C

$[K_3Fe(CN)_6]$ = 2.00×10^{-3} mol dm^{-3}

$[OH^-]$ = 10.0×10^{-2} mol dm^{-3}

[Tetraethylene glycol]= 2.00×10^{-2} mol dm^{-3}

[Ru(VI)] = 7.86×10^{-6} mol dm^{-3}

μ = 0.20 mol dm^{-3}

Time min	$Ce(SO_4)_2$ 1.00×10^{-3}M in ml.	$k_0\times10^2$ ml min^{-1}
1	0.42	
5	0.86	11.00
10	1.40	10.80
15	1.94	10.80
20	2.50	11.20
25	3.04	10.80
30	3.56	10.40
35	4.08	10.40
40	4.62	10.80
45	5.18	11.20
50	5.70	10.40
T∞	10.00	

Average $k_0 = 10.78\times10^{-2}$ ml min^{-1}

A.D. = ± 2.11%

$k_s = 21.56\times10^{-6}$ mol dm^{-3} min^{-1}

$\left(-\frac{dc}{dt}\right) = 21.59\times10^{-6}$ mole dm^{-3} min^{-1}

Table 3.76

Temp. = 35°C

$[K_3Fe(CN)_6]$ = 2.00×10^{-3} mol dm^{-3}

$[OH^-]$ = 10.0×10^{-2} mol dm^{-3}

[Tetraethylene glycol]= 2.00×10^{-2} mol dm^{-3}

[Ru(VI)] = 9.82×10^{-6} mol dm^{-3}

μ = 0.20 mol dm^{-3}

Time min	$Ce(SO_4)_2$ 1.00×10^{-3}M in ml.	$k_0\times10^2$ ml min^{-1}
1	0.48	
3	0.76	14.00
6	1.18	14.00
9	1.58	13.30
12	2.00	14.00
15	2.42	14.00
18	2.82	13.30
21	3.22	13.30
24	3.62	13.30
27	4.02	13.30
30	4.42	13.30
T∞	10.00	

Average $k_0 = 13.58\times10^{-2}$ ml min^{-1}

A.D. = ± 2.47%

$k_s = 27.16\times10^{-6}$ mol dm^{-3} min^{-1}

$\left(-\frac{dc}{dt}\right) = 27.10\times10^{-6}$ mole dm^{-3} min^{-1}

Table 3.77

Temp. = 35°C

$[K_3Fe(CN)_6]$ = 2.00×10^{-3} mol dm^{-3}

$[OH^-]$ = 10.0×10^{-2} mol dm^{-3}

[Tetraethylene glycol]= 2.00×10^{-2} mol dm^{-3}

[Ru(VI)] = 11.79×10^{-6} mol dm^{-3}

μ = 0.20 mol dm^{-3}

Time min	$Ce(SO_4)_2$ 1.00×10^{-3}M in ml.	$k_0\times10^2$ ml min^{-1}
1	0.52	
3	0.86	17.00
6	1.36	16.60
9	1.86	16.60
12	2.34	16.00
15	2.86	17.30
18	3.36	16.60
21	3.86	16.60
24	4.34	16.00
27	4.82	16.00
30	5.32	16.60
T_∞	10.00	

Average $k_0 = 16.43\times10^{-2}$ ml min^{-1}

A.D. = ± 2.17%

$k_s = 32.86\times10^{-6}$ mol dm^{-3} min^{-1}

$\left(-\frac{dc}{dt}\right) = 32.80\times10^{-6}$ mole dm^{-3} min^{-1}

Table 3.78

Temp. = 35°C

$[K_3Fe(CN)_6]$ = 2.00×10^{-3} mol dm^{-3}

$[OH^-]$ = 10.0×10^{-2} mol dm^{-3}

[Tetraethylene glycol]= 2.00×10^{-2} mol dm^{-3}

[Ru(VI)] = 13.10×10^{-6} mol dm^{-3}

μ = 0.20 mol dm^{-3}

Time min	$Ce(SO_4)_2$ 1.00×10^{-3}M in ml.	$k_0\times10^2$ ml min^{-1}
1	0.56	
3	0.94	19.00
6	1.50	18.60
9	2.08	19.30
12	2.66	19.30
15	3.22	18.60
18	3.78	18.60
21	4.32	18.00
24	4.86	18.00
27	5.40	18.00
30	5.94	18.00
T∞	10.00	

Average $k_0 = 18.54\times10^{-2}$ ml min^{-1}

A.D. = ± 2.33%

$k_s = 37.08\times10^{-6}$ mol dm^{-3} min^{-1}

$\left(-\frac{dc}{dt}\right) = 37.14\times10^{-6}$ mole dm^{-3} min^{-1}

Table 3.79

Temp. = 35°C
$[K_3Fe(CN)_6]$ = 2.00×10^{-3} mol dm^{-3}
$[OH^-]$ = 10.00×10^{-2} mol dm^{-3}
[Tetraethylene glycol] = 2.00×10^{-2} mol dm^{-3}
μ = 0.20 mol dm^{-3}

$[Ru(VI)]\times10^6$ mol dm^{-3}	$k_s\times10^6$ mol dm^{-3} min^{-1}	$\left(-\frac{dc}{dt}\right)\times10^6$ mol dm^{-3} min^{-1}	$\frac{k_s}{[Ru(VI)]}$ min^{-1}
3.27	8.54	8.56	2.61
6.55	18.20	18.56	2.77
7.86	21.56	21.59	2.74
9.82	27.16	27.10	2.76
11.79	32.86	32.80	2.78
13.10	37.08	37.14	2.83

Table 3.80

Temp. = 35°C
$[K_3Fe(CN)_6]$ = 2.00×10^{-3} mol dm^{-3}
$[OH^-]$ = 10.00×10^{-2} mol dm^{-3}
[Tetraethylene glycol] = 4.00×10^{-2} mol dm^{-3}
μ = 0.20 mol dm^{-3}

$[Ru(VI)]\times10^6$ mol dm^{-3}	$k_s\times10^6$ mol dm^{-3} min^{-1}	$\left(-\frac{dc}{dt}\right)\times10^6$ mol dm^{-3} min^{-1}	$\frac{k_s}{[Ru(VI)]}$ min^{-1}
3.27	16.01	16.21	4.89
6.55	32.52	32.62	4.96
7.86	38.70	38.40	4.92
9.82	48.62	48.54	4.95
11.79	59.50	59.15	5.04
13.10	66.54	66.26	5.07

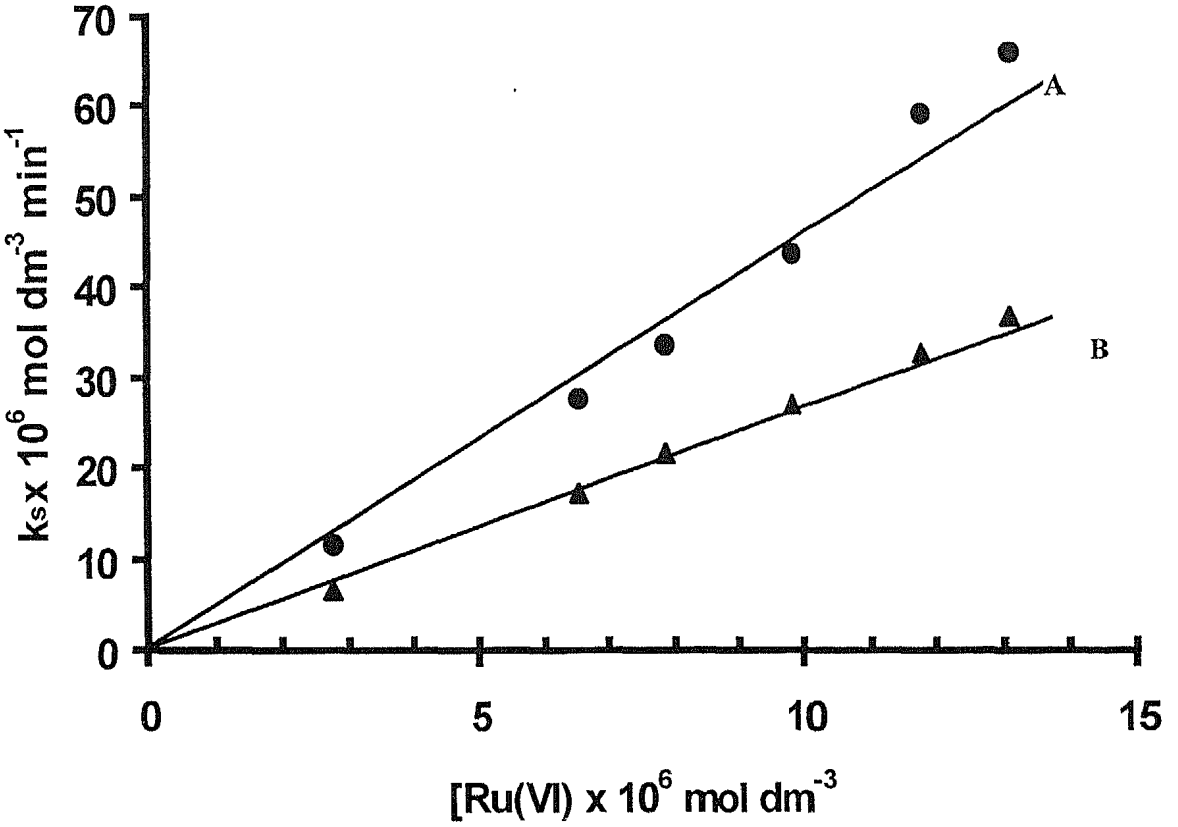


Figure 3.10 Temp. = 35°C; $[K_3Fe(CN)_6] = 2.00 \times 10^{-3}$ mol dm^{-3}; $[OH^-] = 10 \times 10^{-2}$ mol dm^{-3}; [Tetra ethylene Glycol]= (A) 4.00×10^{-2} mol dm^{-3}, (B) 2.0×10^{-2} mol dm^{-3}; $\mu = 0.20$ mol dm^{-3}

3.3 EFFECT OF VARIATION OF THE CONCENTRATION OF HYDROXIDE ION ON THE REACTION VELOCITY.

In this section the effect of hydroxyl ion concentration on the velocity of the reaction has been studied in detail by keeping the concentration of the other reactions and ionic strength constant. The ionic strength was kept constant by the addition of potassium chloride in each set of the reaction.

In each compound the order of the reaction was found out with respect to hexacyanoferrate (III). The standard zero order rate constant (ks) and the velocity (–dc/dt) were calculated as described in section 3.1.

The reaction were studied at lower concentration of sodium hydroxide because at higher concentration of sodium hydroxide, the uncatalysed oxidation of organic compounds may also be significant. In the light of these observations the detailed results are described as follows:

4-methyl pentanol-2 has been taken as the first compound to study the effect by changing the concentration of hydroxyl ion and keeping the concentration of other reactants constant at 35°C. The experimental data thus obtained for individual runs of sodium hydroxide concentration variation are given in the tables 3.81 to 3.86. The summerised results are given in table 3.87. Similar experiment have been performed at other concentration of the 4-methyl pentanol-2 and summarised results are presented in table 3.88. These results have been reproduced in the form of graphs (fig. 3.11(A) and 3.11(B)), which clearly indicate that the velocity of the reaction increases with decrease in the hydroxyl ion concentration.

Table 3.81

Temp. = 35°C
$[K_3Fe(CN)_6]$ = 2.00×10^{-3} mol dm^{-3}
$[OH^-]$ = 25×10^{-2} mol dm^{-3}
[4-methyl pentanol-2] = 4.00×10^{-2} mol dm^{-3}
[Ru(VI)] = 2.18×10^{-6} mol dm^{-3}
μ = 0.25 mole dm^{-3}

Time min	$Ce(SO_4)_2$ 1.25×10^{-3}M in ml.	$k_0\times10^2$ ml min^{-1}
1	0.56	
5	0.80	6.00
10	1.10	6.00
20	1.70	6.00
30	2.32	6.20
40	3.00	6.80
50	3.64	6.40
60	4.30	6.60
70	4.94	6.40
80	5.54	6.00
90	6.00	4.60*
T_∞	8.00	

Average $k_0 = 6.4\times10^{-2}$ ml min^{-1}
A.D. = ± 4.06%
$k_s = 16.00\times10^{-6}$ mol dm^{-3} min^{-1}
$\left(-\frac{dc}{dt}\right) = 16.28\times10^{-6}$ mole dm^{-3} min^{-1}

Table 3.82

Temp. = 35°C
$[K_3Fe(CN)_6]$ = 2.00×10^{-3} mol dm^{-3}
$[OH^-]$ = 20×10^{-2} mol dm^{-3}
[4-methyl pentanol-2] = 4.00×10^{-2} mol dm^{-3}
[Ru(VI)] = 2.18×10^{-6} mol dm^{-3}
μ = 0.25 mole dm^{-3}

Time min	$Ce(SO_4)_2$ 1.25×10^{-3}M in ml.	$k_0\times10^2$ ml min^{-1}
1	0.56	
5	0.86	7.5
10	1.24	7.6
15	1.66	8.4
20	2.10	8.8
30	2.84	7.4
40	3.60	7.6
50	4.36	7.6
60	5.18	8.2
70	6.00	8.2
80	6.60	6.0*
T_∞	8.00	

Average $k_0 = 8.00\times10^{-2}$ ml min^{-1}
A.D. = ± 5.37%
$k_s = 20.00\times10^{-6}$ mol dm^{-3} min^{-1}
$\left(-\frac{dc}{dt}\right) = 20.16\times10^{-6}$ mole dm^{-3} min^{-1}

Table 3.83

Temp. = 35°C

$[K_3Fe(CN)_6]$ = 2.00×10^{-3} mol dm^{-3}

$[OH^-]$ = 15.15×10^{-2} mol dm^{-3}

[4-methyl pentanol-2] = 4.00×10^{-2} mol dm^{-3}

[Ru(VI)] = 2.18×10^{-6} mol dm^{-3}

μ = 0.25 mol dm^{-3}

Time min	$Ce(SO_4)_2$ 1.25×10^{-3}M in ml.	$k_0\times10^2$ ml min^{-1}
1	0.70	
3	0.92	11.0
6	1.24	10.6
9	1.56	10.6
12	1.90	11.3
15	2.20	10.0
20	2.70	10.0
25	3.24	10.8
30	3.80	11.2
35	4.36	11.2
40	4.86	10.0
T_∞	8.00	

Average $k_0 = 10.67\times10^{-2}$ ml min^{-1}

A.D. = ± 4.02%

$k_s = 26.67\times10^{-6}$ mol dm^{-3} min^{-1}

$\left(-\frac{dc}{dt}\right) = 26.70\times10^{-6}$ mole dm^{-3} min^{-1}

Table 3.84

Temp. = 35°C

$[K_3Fe(CN)_6]$ = 2.00×10^{-3}mol dm^{-3}

$[OH^-]$ = 12.5×10^{-2} mol dm^{-3}

[4-methyl pentanol-2] = 4.00×10^{-2} mol dm^{-3}

[Ru(VI)] = 2.18×10^{-6} mol dm^{-3}

μ = 0.25 mol dm^{-3}

Time min	$Ce(SO_4)_2$ 1.25×10^{-3}M in ml.	$k_0\times10^2$ ml min^{-1}
1	0.76	
3	1.00	12.0
6	1.36	12.0
9	1.74	12.6
12	2.10	12.0
15	2.46	12.0
20	3.10	12.8
25	3.60	12.0
30	4.24	12.8
35	4.86	12.4
40	5.46	12.0
T_∞	8.00	

Average $k_0 = 12.38\times10^{-2}$ ml min^{-1}

A.D. = ± 2.7%

$k_s = 30.95\times10^{-6}$ mol dm^{-3} min^{-1}

$\left(-\frac{dc}{dt}\right) = 30.80\times10^{-6}$ mole dm^{-3} min^{-1}

Table 3.85

Temp. = 35°C
$[K_3Fe(CN)_6]$ = 2.00×10^{-3} mol dm^{-3}
$[OH^-]$ = 8.3×10^{-2} mol dm^{-3}
[4-methyl pentanol-2] = 4.00×10^{-2} mol dm^{-3}
[Ru(VI)] = 2.18×10^{-6} mol dm^{-3}
μ = 0.25 mol dm^{-3}

Time min	$Ce(SO_4)_2$ 1.25×10^{-3}M in ml.	$k_0\times10^2$ ml min^{-1}
1	0.84	
3	1.14	15.0
6	1.60	15.3
9	2.06	15.3
12	2.50	14.6
15	2.96	15.3
18	3.40	14.6
21	3.82	14.0
24	4.28	15.3
27	4.70	14.0
30	5.12	14.0
T_∞	8.00	

Average $k_0 = 14.71\times10^{-2}$ ml min^{-1}
A.D. = ± 3.39%
$k_s = 36.77\times10^{-6}$ mol dm^{-3} min^{-1}
$\left(-\frac{dc}{dt}\right) = 36.17\times10^{-6}$ mole dm^{-3} min^{-1}

Table 3.86

Temp. = 35°C
$[K_3Fe(CN)_6]$ = 2.00×10^{-3} mol dm^{-3}
$[OH^-]$ = 6.25×10^{-2} mol dm^{-3}
[4-methyl pentanol-2] = 4.00×10^{-2} mol dm^{-3}
[Ru(VI)] = 2.18×10^{-6} mol dm^{-3}
μ = 0.25 mol dm^{-3}

Time min	$Ce(SO_4)_2$ 1.25×10^{-3}M in ml.	$k_0\times10^2$ ml min^{-1}
1	0.86	
3	1.24	19.0
6	1.80	18.6
9	2.34	18.0
12	2.90	18.6
15	3.46	18.6
18	4.00	18.0
21	4.52	17.3
24	5.04	17.3
27	5.58	17.3
30	6.00	12.0*
T_∞	8.00	

Average $k_0 = 18.1\times10^{-2}$ ml min^{-1}
A.D. = ± 2.76%
$k_s = 45.25\times10^{-6}$ mol dm^{-3} min^{-1}
$\left(-\frac{dc}{dt}\right) = 45.20\times10^{-6}$ mole dm^{-3} min^{-1}

Table 3.87

Temp. = 35°C
$[K_3Fe(CN)_6]$ = 2.00×10^{-3} mol dm^{-3}
[Ru(VI)] = 2.18×10^{-6} mol dm^{-3}
[4-methyl-pentanol-2] = 4.00×10^{-2} mol dm^{-3}
μ = 0.25 mol dm^{-3}

$[OH^-]\times10^2$ mol dm^{-3}	$k_s\times10^6$ mol dm^{-3} min^{-1}	$\left(-\frac{dc}{dt}\right)\times10^6$ mol dm^{-3} min^{-1}
25.00	16.00	16.28
20.00	20.00	20.16
15.60	26.67	26.70
12.50	30.95	30.80
8.33	36.77	36.17
6.25	45.25	45.20

Table 3.88

Temp. = 35°C
$[K_3Fe(CN)_6]$ = 2.00×10^{-3} mol dm^{-3}
[Ru(VI)] = 2.18×10^{-6} mol dm^{-3}
[4-methyl pentanol-2] = 6.32×10^{-2} mol dm^{-3}
μ = 0.25 mol dm^{-3}

$[OH^-]\times10^2$ mol dm^{-3}	$k_s\times10^6$ mol dm^{-3} min^{-1}	$\left(-\frac{dc}{dt}\right)\times10^6$ mol dm^{-3} min^{-1}
25.00	31.00	31.20
20.00	33.50	33.15
15.60	40.87	40.38
12.50	45.75	46.00
8.33	58.00	58.18
6.25	66.00	65.98

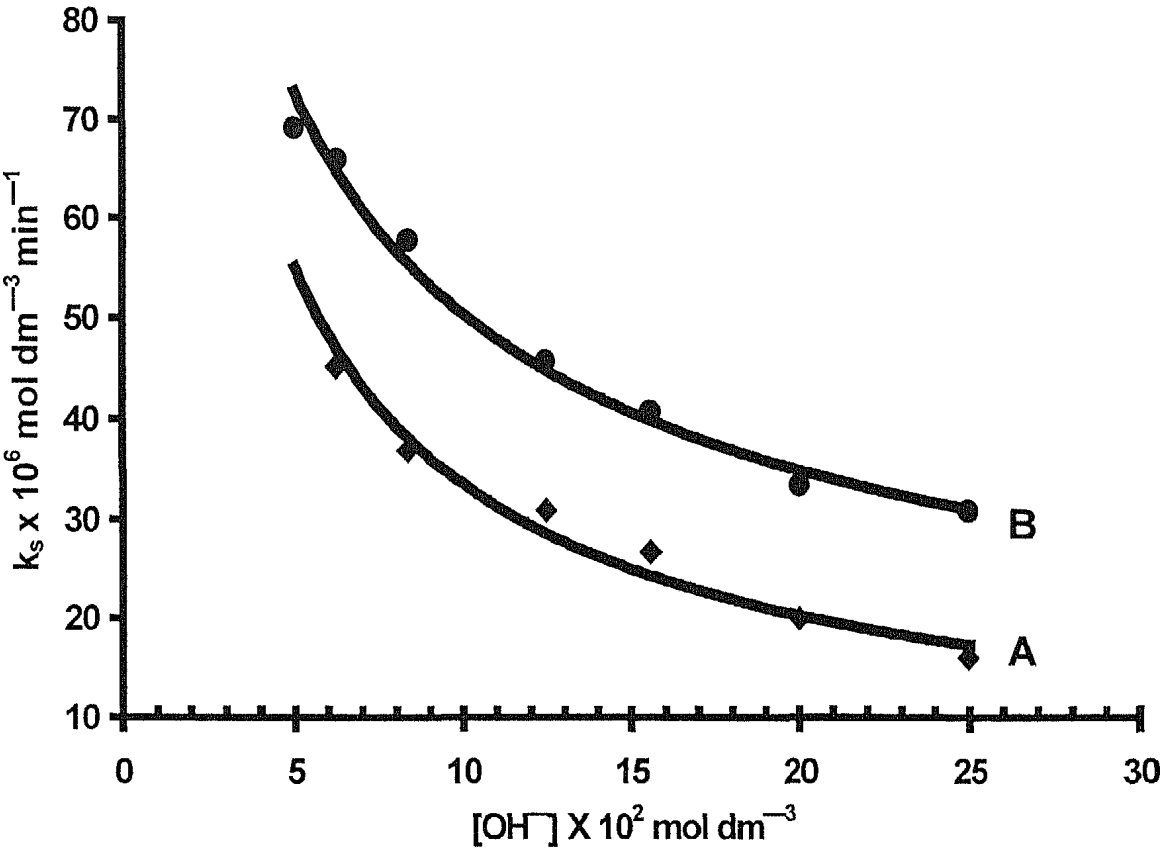


Figure 3.11 $[K_3Fe(CN)_6] = 2.00 \times 10^{-3}$ mol dm^{-3}; [Ru(VI)] = 2.18×10^{-6} mol dm^{-3} ; [4-Methyl Pentanol-2] (A) = 4.00×10^{-2} mol dm^{-3} (B) = 6.32×10^{-2} mol dm^{-3}; μ = 0.25 mol dm^{-3}, Temp.= 35°C.;

Effect of the variation of the concentration of hydroxyl ion in the reaction velocity in case of 2-methoxy ethanol.

2-methoxy ethanol has been taken the second compound to study the effect of hydroxide ion on the reaction velocity. Observation were made by changing the concentration of hydroxyl-ion, keeping the concentration of the other reactants constant. The result thus obtained are given in tables (3.89 to 3.94) and the summarised results are presented in (3.95). Similar experiments were performed at other concentration of 2-methoxy ethanol and results thus obtained are summarised in the table (3.96).

In each case the velocity (–dc/dt) is calculated from the zero order plots and summarised results are given in the table 3.95 and 3.96. These results have been reproduced in the form of graphs fig. 3.12(A) and 3.12(B) which clearly indicate that the velocity of reaction increases with decrease in sodium hydroxide concentration.

Table 3.89

Temp. = 35°C

$[K_3Fe(CN)_6]$ = 2.00×10^{-3} mol dm^{-3}

$[OH^-]$ = 20×10^{-2} mol dm^{-3}

[2-methoxy ethanol] = 5.00×10^{-2} mol dm^{-3}

[Ru(VI)] = 15.5×10^{-7} mol dm^{-3}

μ = 0.20 mole dm^{-3}

Time min	$Ce(SO_4)_2$ 1.00×10^{-3}M in ml.	$k_0\times10^2$ ml min^{-1}
1	0.42	
5	0.88	11.5
10	1.46	11.6
15	2.02	11.2
20	2.58	11.2
25	3.16	11.6
30	3.72	11.2
35	4.26	10.8
40	4.80	10.8
45	5.34	10.8
50	5.86	10.4
T_∞	10.00	

Average $k_0 = 11.11\times10^{-2}$ ml min^{-1}

A.D. = ± 2.95%

$k_s = 22.20\times10^{-6}$ mol dm^{-3} min^{-1}

$\left(-\frac{dc}{dt}\right) = 22.48\times10^{-6}$ mole dm^{-3} min^{-1}

Table 3.90

Temp. = 35°C

$[K_3Fe(CN)_6]$ = 2.00×10^{-3} mol dm^{-3}

$[OH^-]$ = 15×10^{-2} mol dm^{-3}

[2-methoxy ethanol] = 5.00×10^{-2} mol dm^{-3}

[Ru(VI)] = 15.5×10^{-7} mol dm^{-3}

μ = 0.20 mole dm^{-3}

Time min	$Ce(SO_4)_2$ 1.00×10^{-3}M in ml.	$k_0\times10^2$ ml min^{-1}
1	0.44	
5	1.00	14.0
10	1.70	14.0
15	2.38	13.6
20	3.08	14.0
25	3.76	13.6
30	4.44	13.6
35	5.10	13.2
40	5.76	13.2
45	6.40	12.8
50	7.04	12.8
T_∞	10.00	

Average $k_0 = 13.5\times10^{-2}$ ml min^{-1}

A.D. = ± 2.81%

$k_s = 27.0\times10^{-6}$ mol dm^{-3} min^{-1}

$\left(-\frac{dc}{dt}\right) = 27.24\times10^{-6}$ mole dm^{-3} min^{-1}

Table 3.91

Temp. = 35°C
$[K_3Fe(CN)_6]$ = 2.00×10^{-3} mol dm^{-3}
$[OH^-]$ = 10.00×10^{-2} mol dm^{-3}
[2-methoxy ethanol] = 5.00×10^{-2} mol dm^{-3}
[Ru(VI)] = 15.5×10^{-7} mol dm^{-3}
μ = 0.20 mol dm^{-3}

Time min	$Ce(SO_4)_2$ 1.00×10^{-3}M in ml.	$k_0\times10^2$ ml min^{-1}
1	0.80	
3	1.20	20.0
6	1.82	20.6
9	2.44	20.6
12	3.04	20.0
15	3.64	20.0
18	4.24	20.0
21	4.82	19.3
24	5.40	19.3
27	5.98	19.3
30	6.56	19.3
T_∞	10.00	

Average $k_0 = 19.8\times10^{-2}$ ml min^{-1}
A.D. = ± 2.22%
$k_s = 39.6\times10^{-6}$ mol dm^{-3} min^{-1}
$\left(-\frac{dc}{dt}\right) = 39.68\times10^{-6}$ mole dm^{-3} min^{-1}

Table 3.92

Temp. = 35°C
$[K_3Fe(CN)_6]$ = 2.00×10^{-3}mol dm^{-3}
$[OH^-]$ = 6.66×10^{-2} mol dm^{-3}
[2-methoxy ethanol] = 5.00×10^{-2} mol dm^{-3}
[Ru(VI)] = 15.5×10^{-7} mol dm^{-3}
μ = 0.20 mol dm^{-3}

Time min	$Ce(SO_4)_2$ 1.00×10^{-3}M in ml.	$k_0\times10^2$ ml min^{-1}
1	0.84	
3	1.32	24.0
5	1.80	24.0
7	2.28	24.0
9	2.74	23.0
11	3.22	24.0
13	3.68	23.0
15	4.14	23.0
17	4.62	24.0
19	5.08	23.0
21	5.54	23.0
T_∞	10.00	

Average $k_0 = 23.5\times10^{-2}$ ml min^{-1}
A.D. = ± 2.12%
$k_s = 47.0\times10^{-6}$ mol dm^{-3} min^{-1}
$\left(-\frac{dc}{dt}\right) = 47.22\times10^{-6}$ mole dm^{-3} min^{-1}

Table 3.93

Temp. = 35°C

$[K_3Fe(CN)_6]$ = 2.00×10^{-3} mol dm^{-3}

$[OH^-]$ = 5.00×10^{-2} mol dm^{-3}

[2-methoxy ethanol] = 5.00×10^{-2} mol dm^{-3}

[Ru(VI)] = 15.5×10^{-7} mol dm^{-3}

μ = 0.20 mol dm^{-3}

Time min	$Ce(SO_4)_2$ 1.00×10^{-3}M in ml.	$k_0\times10^2$ ml min^{-1}
1	0.96	
2	1.24	28.0
4	1.80	28.0
6	2.34	27.0
8	2.88	27.0
10	3.44	28.0
12	4.00	28.0
14	4.54	27.0
16	5.08	27.0
18	5.62	27.0
20	6.18	28.0
T_∞	10.00	

Average $k_0 = 27.5\times10^{-2}$ ml min^{-1}

A.D. = ± 1.81%

$k_s = 55.0\times10^{-6}$ mol dm^{-3} min^{-1}

$\left(-\frac{dc}{dt}\right) = 54.82\times10^{-6}$ mole dm^{-3} min^{-1}

Table 3.94

Temp. = 35°C

$[K_3Fe(CN)_6]$ = 2.00×10^{-3} mol dm^{-3}

$[OH^-]$ = 2.5×10^{-2} mol dm^{-3}

[2-methoxy ethanol] = 5.00×10^{-2} mol dm^{-3}

[Ru(VI)] = 15.5×10^{-7} mol dm^{-3}

μ = 0.20 mol dm^{-3}

Time min	$Ce(SO_4)_2$ 1.00×10^{-3}M in ml.	$k_0\times10^2$ ml min^{-1}
1	1.02	
2	1.38	36.0
4	2.10	36.0
6	2.80	35.0
8	3.50	35.0
10	4.20	35.0
12	4.90	35.0
14	5.60	35.0
16	6.38	34.0
18	6.96	34.0
20	7.40	22.00*
T_∞	10.00	

Average $k_0 = 35.5\times10^{-2}$ ml min^{-1}

A.D. = ± 2.02%

$k_s = 71.0\times10^{-6}$ mol dm^{-3} min^{-1}

$\left(-\frac{dc}{dt}\right) = 70.97\times10^{-6}$ mole dm^{-3} min^{-1}

Table 3.95

Temp. = 35°C
$[K_3Fe(CN)_6]$ = 2.00×10^{-3} mol dm^{-3}
[2-methoxy ethanol] = 5.00×10^{-2} mol dm^{-3}
[Ru(VI)] = 15.5×10^{-7} mol dm^{-3}
μ = 0.20 mol dm^{-3}

$[OH^-]\times10^2$ mol dm^{-3}	$k_s\times10^6$ mol dm^{-3} min^{-1}	$\left(-\frac{dc}{dt}\right)\times10^6$ mol dm^{-3} min^{-1}
20.0	22.20	22.48
15.1	27.00	27.24
10.0	39.60	39.68
6.6	47.00	47.22
5.0	55.00	54.82
2.5	71.00	70.97

Table 3.96

Temp. = 35°C
$[K_3Fe(CN)_6]$ = 2.00×10^{-3} mol dm^{-3}
[Ru(VI)] = 15.5×10^{-7} mol dm^{-3}
[4-methoxy-ethanol] = 2.50×10^{-2} mol dm^{-3}
μ = 0.20 mol dm^{-3}

$[OH^-]\times10^2$ mol dm^{-3}	$k_s\times10^6$ mol dm^{-3} min^{-1}	$\left(-\frac{dc}{dt}\right)\times10^6$ mol dm^{-3} min^{-1}
20.0	13.40	13.68
15.1	16.20	16.12
10.0	21.40	21.46
6.6	25.10	25.52
5.0	28.00	27.86
2.5	37.00	36.92

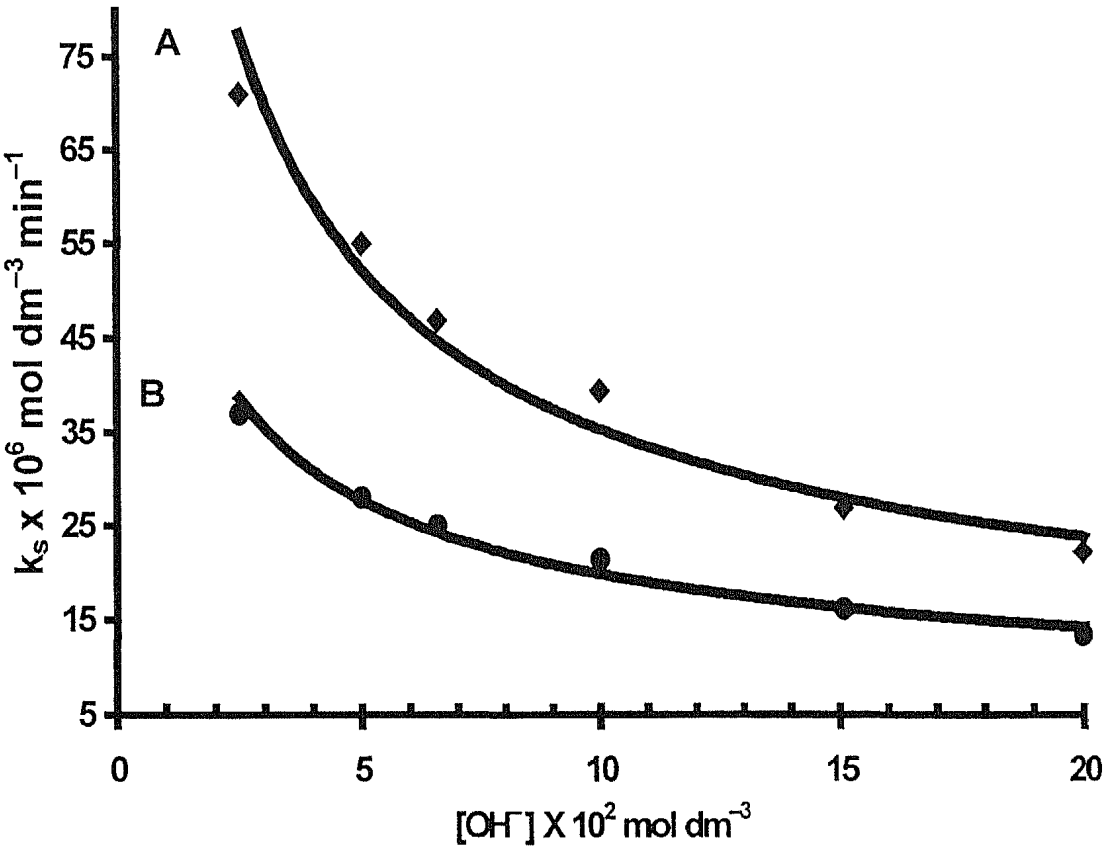


Figure 3.12 $[K_3Fe(CN)_6] = 2.00 \times 10^{-3}$ mol dm^{-3}; [Ru(VI)] = 15.5×10^{-7} mol dm^{-3} ; [4-Methoxy Ethanol] (A) = 5.00×10^{-2} mol dm^{-3} (B) = 2.5×10^{-2} mol dm^{-3}; μ = 0.25 mol dm^{-3}, Temp.= 35°C.;

Effect of variation of the concentration of hydroxide ion on the reaction velocity in case of diethylene glycol.

Diethylene glycol has been taken the third compound to study the effect of hydroxyl ion on the reaction velocity observation were made by changing the concentration of hydroxyl ion keeping the concentration of the other reactants constant. The results thus obtained are given in tables (3.97 to 3.102) and the summarised results are presented in table (3.103). Similar experiments were performed at other concentration of diethylene glycol and results thus obtained are summarised in the table (3.104).

In each case the velocity (–dc/dt) is calculated from zero order plots and summarised results are given in the tables (3.103, 3.104). These results have been reproduced in the form of graphs (fig. 3.13(A) and 3.13(B)) which clearly indicate that the velocity of reaction increases with decrease in sodium hydroxide concentration.

Table 3.97

Temp. = 30°C
$[K_3Fe(CN)_6]$ = 2.00×10^{-3} mol dm^{-3}
$[OH^-]$ = 2×10^{-1} mol dm^{-3}
[Diethylene glycol] = 2.00×10^{-2} mol dm^{-3}
[Ru(VI)] = 3.66×10^{-6} mol dm^{-3}
μ = 0.25 mole dm^{-3}

Time min	$Ce(SO_4)_2$ 1.00×10^{-3}M in ml.	$k_0\times10^2$ ml min^{-1}
1	0.26	
6	0.52	5.2
14	0.96	5.5
24	1.46	5.0
34	1.96	5.0
44	2.48	5.2
54	3.00	5.2
64	3.52	5.2
74	4.04	5.2
84	4.56	5.2
94	5.08	5.2
T_∞	10.00	

Average $k_0 = 5.19\times10^{-2}$ ml min^{-1}
A.D. = ± 1.65%
$k_s = 10.38\times10^{-6}$ mol dm^{-3} min^{-1}
$\left(-\frac{dc}{dt}\right) = 10.44\times10^{-6}$ mole dm^{-3} min^{-1}

Table 3.98

Temp. = 30°C
$[K_3Fe(CN)_6]$ = 2.00×10^{-3} mol dm^{-3}
$[OH^-]$ = 1.0×10^{-1} mol dm^{-3}
[Diethylene glycol] = 2.00×10^{-2} mol dm^{-3}
[Ru(VI)] = 3.66×10^{-6} mol dm^{-3}
μ = 0.25 mole dm^{-3}

Time min	$Ce(SO_4)_2$ 1.00×10^{-3}M in ml.	$k_0\times10^2$ ml min^{-1}
1	0.28	
6	0.72	8.8
11	1.16	8.8
16	1.58	8.4
26	2.50	9.2
36	3.36	8.6
46	4.26	9.0
56	5.16	9.0
66	6.00	8.4
76	6.90	9.0
86	7.38	4.8*
T_∞	10.00	

Average $k_0 = 9.24\times10^{-2}$ ml min^{-1}
A.D. = ± 4.76%
$k_s = 18.48\times10^{-6}$ mol dm^{-3} min^{-1}
$\left(-\frac{dc}{dt}\right) = 18.74\times10^{-6}$ mole dm^{-3} min^{-1}

Table 3.99

Temp. = 30°C

$[K_3Fe(CN)_6]$ = 2.00×10^{-3} mol dm^{-3}

$[OH^-]$ = 5.00×10^{-2} mol dm^{-3}

[Diethylene glycol] = 2.00×10^{-2} mol dm^{-3}

[Ru(VI)] = 3.66×10^{-6} mol dm^{-3}

μ = 0.25 mol dm^{-3}

Time min	$Ce(SO_4)_2$ 1.00×10^{-3}M in ml.	$k_0\times10^2$ ml min^{-1}
1	0.30	
5	0.80	12.5
9	1.28	12.0
13	1.80	13.0
18	2.42	12.4
23	3.04	12.4
28	3.68	12.8
33	4.28	12.0
38	4.88	12.0
42	5.38	12.5
47	5.98	12.0
T_∞	10.00	

Average $k_0 = 12.36\times10^{-2}$ ml min^{-1}

A.D. = ± 2.33%

$k_s = 24.72\times10^{-6}$ mol dm^{-3} min^{-1}

$\left(-\frac{dc}{dt}\right) = 24.48\times10^{-6}$ mole dm^{-3} min^{-1}

Table 3.100

Temp. = 30°C

$[K_3Fe(CN)_6]$ = 2.00×10^{-3}mol dm^{-3}

$[OH^-]$ = 3.25×10^{-2} mol dm^{-3}

[Diethylene glycol] = 2.00×10^{-2} mol dm^{-3}

[Ru(VI)] = 3.66×10^{-6} mol dm^{-3}

μ = 0.25 mol dm^{-3}

Time min	$Ce(SO_4)_2$ 1.00×10^{-3}M in ml.	$k_0\times10^2$ ml min^{-1}
1	0.32	
5	0.90	14.5
10	1.66	15.2
15	2.40	14.8
20	3.14	14.8
25	3.86	14.4
30	4.58	14.4
35	5.32	14.8
40	6.06	14.8
45	6.82	15.2
50	7.32	10.0*
T_∞	10.00	

Average $k_0 = 14.76\times10^{-2}$ ml min^{-1}

A.D. = ± 1.51%

$k_s = 29.52\times10^{-6}$ mol dm^{-3} min^{-1}

$\left(-\frac{dc}{dt}\right) = 29.12\times10^{-6}$ mole dm^{-3} min^{-1}

Table 3.101

Temp. = 30°C
$[K_3Fe(CN)_6]$ = 2.00×10^{-3} mol dm^{-3}
$[OH^-]$ = 2.5×10^{-2} mol dm^{-3}
[Diethylene glycol] = 2.00×10^{-2} mol dm^{-3}
[Ru(VI)] = 3.66×10^{-6} mol dm^{-3}
μ = 0.25 mol dm^{-3}

Time min	$Ce(SO_4)_2$ 1.00×10^{-3}M in ml.	$k_0\times10^2$ ml min^{-1}
1	0.30	
5	0.94	16.0
10	1.78	16.8
14	2.42	16.0
18	3.06	15.0
22	3.72	16.5
26	4.38	16.5
30	5.04	16.5
34	5.70	16.5
38	6.30	15.0
42	6.90	15.0
T_∞	10.00	

Average $k_0 = 16.08\times10^{-2}$ ml min^{-1}
A.D. = ± 2.98%
$k_s = 32.16\times10^{-6}$ mol dm^{-3} min^{-1}
$\left(-\frac{dc}{dt}\right) = 32.28\times10^{-6}$ mole dm^{-3} min^{-1}

Table 3.102

Temp. = 30°C
$[K_3Fe(CN)_6]$ = 2.00×10^{-3} mol dm^{-3}
$[OH^-]$ = 2.0×10^{-2} mol dm^{-3}
[Diethylene glycol] = 2.00×10^{-2} mol dm^{-3}
[Ru(VI)] = 3.66×10^{-6} mol dm^{-3}
μ = 0.25 mol dm^{-3}

Time min	$Ce(SO_4)_2$ 1.00×10^{-3}M in ml.	$k_0\times10^2$ ml min^{-1}
1	0.34	
5	1.06	18.0
7	1.44	19.0
11	2.12	17.0
15	2.86	18.5
17	3.22	18.0
21	3.92	17.5
25	4.64	18.0
29	5.34	17.5
33	6.08	18.5
37	6.80	18.0
T_∞	10.00	

Average $k_0 = 18.00\times10^{-2}$ ml min^{-1}
A.D. = ± 2.22%
$k_s = 36.00\times10^{-6}$ mol dm^{-3} min^{-1}
$\left(-\frac{dc}{dt}\right) = 36.34\times10^{-6}$ mole dm^{-3} min^{-1}

Table 3.103

Temp. = 30°C
$[K_3Fe(CN)_6]$ = 2.00×10^{-3} mol dm^{-3}
[Diethylene glycol] = 2.00×10^{-2} mol dm^{-3}
[Ru(VI)] = 3.66×10^{-6} mol dm^{-3}
μ = 0.25 mol dm^{-3}

$[OH^-]\times10^2$ mol dm^{-3}	$k_s\times10^6$ mol dm^{-3} min^{-1}	$\left(-\frac{dc}{dt}\right)\times10^6$ mol dm^{-3} min^{-1}
20.00	10.38	10.44
10.00	18.48	18.74
5.00	24.72	24.48
3.25	29.52	29.12
2.50	32.16	32.28
2.00	36.00	36.34

Table 3.104

Temp. = 30°C
$[K_3Fe(CN)_6]$ = 2.00×10^{-3} mol dm^{-3}
[Diethylene glycol] = 4.00×10^{-2} mol dm^{-3}
[Ru(VI)] = 3.66×10^{-6} mol dm^{-3}
μ = 0.25 mol dm^{-3}

$[OH^-]\times10^2$ mol dm^{-3}	$k_s\times10^6$ mol dm^{-3} min^{-1}	$\left(-\frac{dc}{dt}\right)\times10^6$ mol dm^{-3} min^{-1}
20.00	20.33	20.46
10.00	31.17	31.38
5.00	42.52	41.08
3.25	47.74	47.94
2.50	53.36	53.88
2.00	54.77	54.74

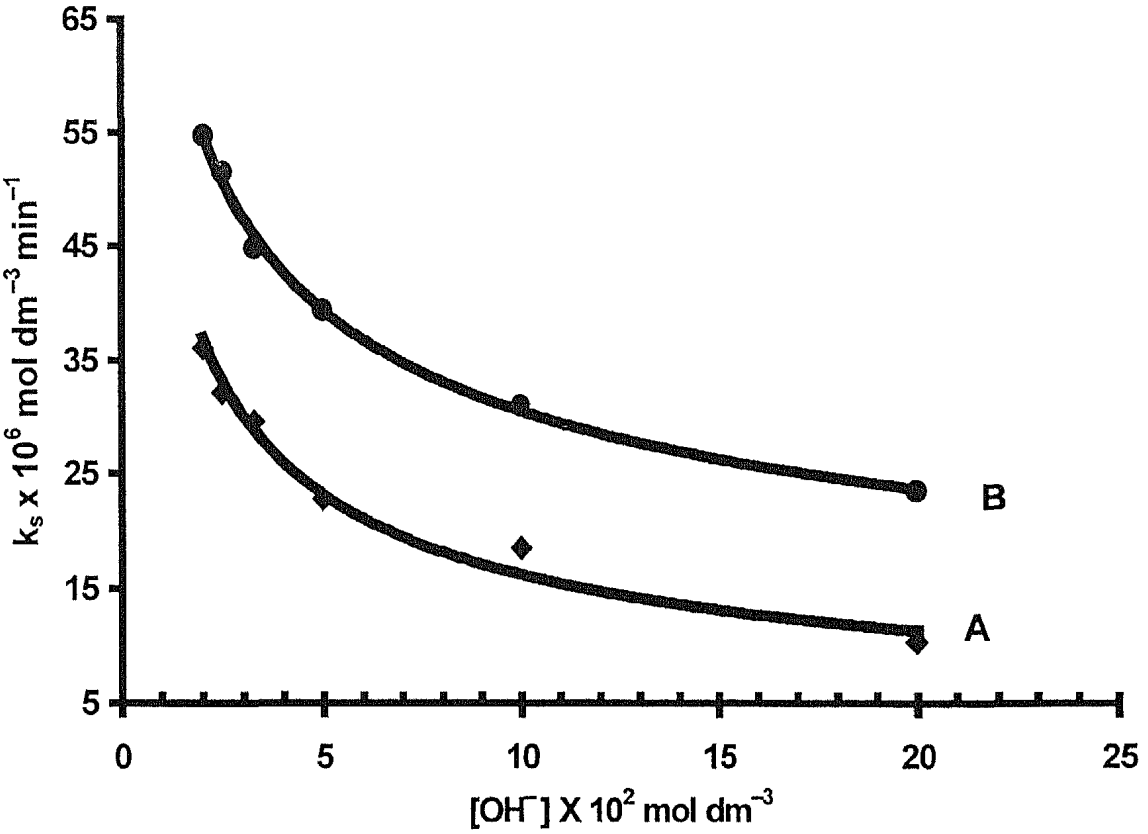


Figure 3.13 $[K_3Fe(CN)_6] = 2.00 \times 10^{-3}$ mol dm^{-3}; [Ru(VI)] = 3.66×10^{-6} mol dm^{-3} ; [Diethylene Glycol] (A) = 2.00×10^{-2} mol dm^{-3} (B) = 4.0×10^{-2} mol dm^{-3}; μ = 0.25 mol dm^{-3}, Temp.= 30°C.;

Effect of variation of concentration of hydroxide ion on the reaction velocity in case of Triethylene glycol.

Triethylene glycol has been taken as the fourth compound to study the effect of hydroxide ion on the reaction velocity observation were made by changing the concentration of hydroxyl ion, keeping the concentration of other reactants constant. The result thus obtained are given in table (3.105 to 3.110) and the summarised results are presented in table (3.111) similar experiments were performed at other concentration of triethylene glycol and the results thus obtained are summarised in the table (3.112).

In each case the velocity (–dc/dt) is calculated from plots made between time Vs remaining concentration of hexacyanoferrate in terms of ceric sulphate and summarised results are given in the tables (3.111, 3.112). These result have been reproduced in the form of graphs fig. 3.14(A) and 3.14(B) which clearly indicates that the velocity of reaction increases with decrease in sodium hydroxide concentration.

Table 3.105

Temp. = 35°C

$[K_3Fe(CN)_6]$ = 2.00×10^{-3} mol dm^{-3}

$[OH^-]$ = 20×10^{-2} mol dm^{-3}

[Triethylene glycol] = 2.50×10^{-2} mol dm^{-3}

[Ru(VI)] = 4.8×10^{-6} mol dm^{-3}

μ = 0.20 mole dm^{-3}

Time min	$Ce(SO_4)_2$ 1.00×10^{-3}M in ml.	$k_0\times10^2$ ml min^{-1}
1	0.52	
5	0.90	9.5
10	1.38	9.6
15	1.86	9.6
20	2.32	9.2
25	2.78	9.2
30	3.26	9.6
35	3.72	9.2
40	4.18	9.2
45	4.64	9.2
T_∞	10.00	

Average $k_0 = 9.36\times10^{-2}$ ml min^{-1}

A.D. = ± 1.96%

$k_s = 18.72\times10^{-6}$ mol dm^{-3} min^{-1}

$\left(-\frac{dc}{dt}\right) = 18.22\times10^{-6}$ mole dm^{-3} min^{-1}

Table 3.106

Temp. = 35°C

$[K_3Fe(CN)_6]$ = 2.00×10^{-3} mol dm^{-3}

$[OH^-]$ = 15.15×10^{-2} mol dm^{-3}

[Triethylene glycol] = 2.50×10^{-2} mol dm^{-3}

[Ru(VI)] = 4.8×10^{-6} mol dm^{-3}

μ = 0.20 mole dm^{-3}

Time min	$Ce(SO_4)_2$ 1.00×10^{-3}M in ml.	$k_0\times10^2$ ml min^{-1}
1	0.58	
5	1.00	10.5
10	1.54	10.8
15	2.08	10.8
20	2.60	10.4
25	3.12	10.4
30	3.62	10.0
35	4.12	10.0
40	4.64	10.4
45	5.14	10.0
T_∞	10.00	

Average $k_0 = 10.3\times10^{-2}$ ml min^{-1}

A.D. = ± 2.52%

$k_s = 20.6\times10^{-6}$ mol dm^{-3} min^{-1}

$\left(-\frac{dc}{dt}\right) = 20.00\times10^{-6}$ mole dm^{-3} min^{-1}

Table 3.107

Temp. = 35°C

$[K_3Fe(CN)_6]$ = 2.00×10^{-3} mol dm^{-3}

$[OH^-]$ = 10.00×10^{-2} mol dm^{-3}

[Triethylene glycol] = 2.50×10^{-2} mol dm^{-3}

[Ru(VI)] = 4.8×10^{-6} mol dm^{-3}

μ = 0.20 mol dm^{-3}

Time min	$Ce(SO_4)_2$ 1.00×10^{-3}M in ml.	$k_0\times10^2$ ml min^{-1}
1	0.64	
4	1.04	13.3
8	1.58	13.5
12	2.12	13.5
16	2.64	13.0
20	3.16	13.0
24	3.70	13.5
28	4.24	13.5
32	4.76	13.0
36	5.28	13.0
40	5.80	13.0
T_∞	10.00	

Average $k_0 = 13.23\times10^{-2}$ ml min^{-1}

A.D. = ± 1.73%

$k_s = 26.46\times10^{-6}$ mol dm^{-3} min^{-1}

$\left(-\frac{dc}{dt}\right) = 26.68\times10^{-6}$ mole dm^{-3} min^{-1}

Table 3.108

Temp. =35°C

$[K_3Fe(CN)_6]$ = 2.00×10^{-3}mol dm^{-3}

$[OH^-]$ = 5.00×10^{-2} mol dm^{-3}

[Triethylene glycol] = 2.50×10^{-2} mol dm^{-3}

[Ru(VI)] = 4.8×10^{-6} mol dm^{-3}

μ = 0.20 mol dm^{-3}

Time min	$Ce(SO_4)_2$ 1.00×10^{-3}M in ml.	$k_0\times10^2$ ml min^{-1}
1	0.72	
4	1.38	22.0
7	2.04	22.0
10	2.68	21.3
13	3.32	21.3
16	3.96	21.3
19	4.60	21.3
21	5.22	20.6
24	5.84	20.6
27	6.46	20.6
30	7.00	18.0*
T_∞	10.00	

Average $k_0 = 21.2\times10^{-2}$ ml min^{-1}

A.D. = ± 1.98%

$k_s = 40.24\times10^{-6}$ mol dm^{-3} min^{-1}

$\left(-\frac{dc}{dt}\right) = 40.08\times10^{-6}$ mole dm^{-3} min^{-1}

Table 3.109

Temp. = 35°C

$[K_3Fe(CN)_6]$ = 2.00×10^{-3} mol dm^{-3}

$[OH^-]$ = 3.3×10^{-2} mol dm^{-3}

[Triethylene glycol] = 2.50×10^{-2} mol dm^{-3}

[Ru(VI)] = 4.8×10^{-6} mol dm^{-3}

μ = 0.20 mol dm^{-3}

Time min	$Ce(SO_4)_2$ 1.00×10^{-3}M in ml.	$k_0\times10^2$ ml min^{-1}
1	0.78	
3	1.34	28.0
6	2.18	28.0
9	3.02	28.0
12	3.86	28.0
15	4.68	27.3
18	5.50	27.3
21	6.32	27.3
24	7.00	22.6*
T_∞	10.00	

Average $k_0 = 27.7\times10^{-2}$ ml min^{-1}

A.D. = ± 1.22%

$k_s = 55.40\times10^{-6}$ mol dm^{-3} min^{-1}

$\left(-\frac{dc}{dt}\right) = 55.36\times10^{-6}$ mole dm^{-3} min^{-1}

Table 3.110

Temp. = 35°C

$[K_3Fe(CN)_6]$ = 2.00×10^{-3} mol dm^{-3}

$[OH^-]$ = 2.5×10^{-2} mol dm^{-3}

[Triethylene glycol] = 2.50×10^{-2} mol dm^{-3}

[Ru(VI)] = 4.8×10^{-6} mol dm^{-3}

μ = 0.20 mol dm^{-3}

Time min	$Ce(SO_4)_2$ 1.00×10^{-3}M in ml.	$k_0\times10^2$ ml min^{-1}
1	0.80	
3	1.42	31.0
5	2.06	32.0
7	2.70	32.0
9	3.32	31.0
11	3.96	32.0
13	4.60	32.0
15	5.24	32.0
17	5.88	32.0
19	6.50	31.0
21	7.00	25.0*
T_∞	10.00	

Average $k_0 = 31.6\times10^{-2}$ ml min^{-1}

A.D. = ± 1.45%

$k_s = 63.20\times10^{-6}$ mol dm^{-3} min^{-1}

$\left(-\frac{dc}{dt}\right) = 63.00\times10^{-6}$ mole dm^{-3} min^{-1}

Table 3.111

Temp. = 35°C
$[K_3Fe(CN)_6]$ = 2.00×10^{-3} mol dm^{-3}
[Triethylene glycol] = 2.50×10^{-2} mol dm^{-3}
[Ru(VI)] = 4.81×10^{-6} mol dm^{-3}
μ = 0.20mol dm^{-3}

$[OH^-]\times10^2$ mol dm^{-3}	$k_s\times10^6$ mol dm^{-3} min^{-1}	$\left(-\frac{dc}{dt}\right)\times10^6$ mol dm^{-3} min^{-1}
20.00	18.72	18.22
15.15	20.60	20.00
10.00	26.48	26.68
5.00	40.24	40.08
3.33	55.40	55.36
2.50	63.20	63.00

Table 3.112

Temp. = 35°C
$[K_3Fe(CN)_6]$ = 2.00×10^{-3} mol dm^{-3}
[Triethylene glycol] = 5.00×10^{-2} mol dm^{-3}
[Ru(VI)] = 4.81×10^{-6} mol dm^{-3}
μ = 0.20 mol dm^{-3}

$[OH^-]\times10^2$ mol dm^{-3}	$k_s\times10^6$ mol dm^{-3} min^{-1}	$\left(-\frac{dc}{dt}\right)\times10^6$ mol dm^{-3} min^{-1}
20.00	36.48	36.88
15.15	40.48	40.68
10.00	47.20	47.00
5.00	62.80	63.00
3.33	84.57	84.96
2.50	91.77	91.80

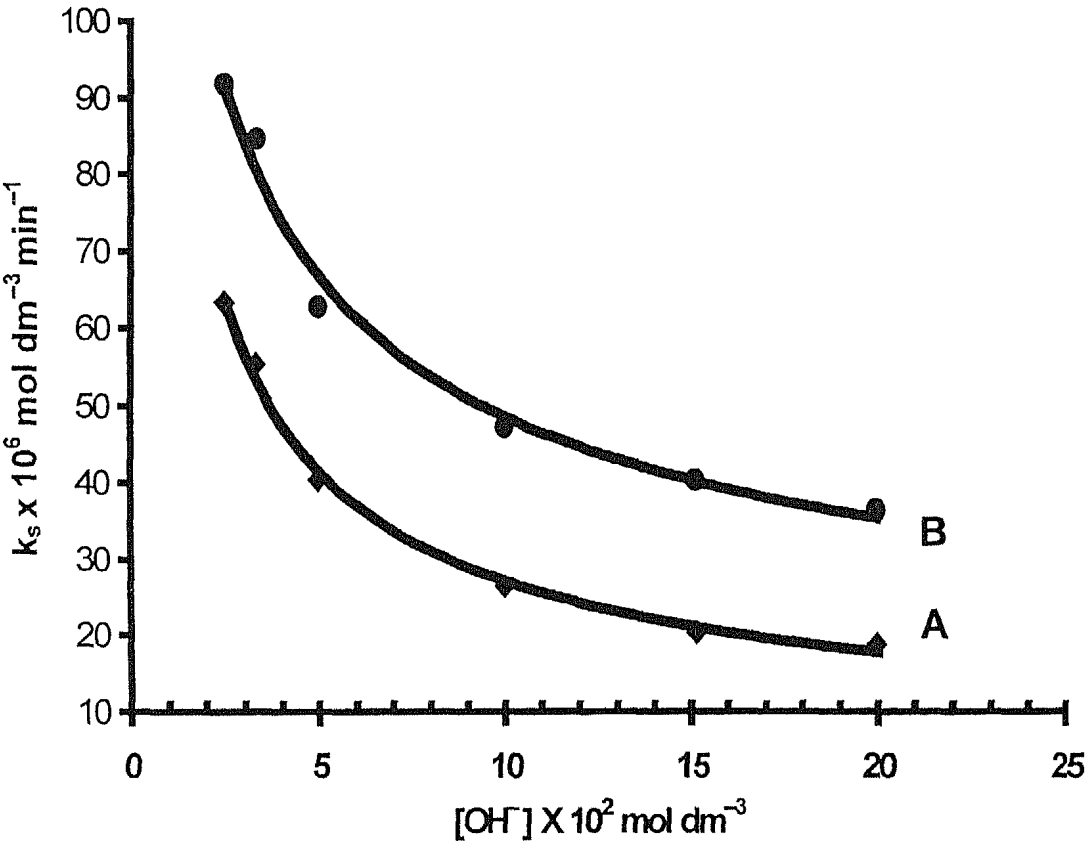


Figure 3.14 $[K_3Fe(CN)_6] = 2.00 \times 10^{-3}$ mol dm^{-3}; [Ru(VI)] = 4.81×10^{-6} mol dm^{-3} ; [Triethylene Glycol] (A) = 2.5×10^{-2} mol dm^{-3} (B) = 5.0×10^{-2} mol dm^{-3}; μ = 0.20 mol dm^{-3}, Temp.= 35°C.;

Effect of variation of concentration of hydroxide ion on the reaction velocity in case of Tetraethylene glycol.

Tetraethylene glycol has been taken as the last compound to study the effect of changing the concentration of hydroxyl ion. The experimental result obtained for individual run of sodium-hydroxide concentration variation are given in the tables (3.113 to 3.118). The summarised results are given in table (3.119). Similar experiment have been performed at other concentration of the tetraethylene glycol are summarised results are presented in table (3.120). The results have been reproduced in the form of graph (fig. 3.15(A) and 3.15(B)), which clearly indicate that the velocity of the reaction increases with decreased in the hydroxyl ion concentration.

Table 3.113

Temp. = 35°C

$[K_3Fe(CN)_6]$ = 2.00×10^{-3} mol dm^{-3}

$[OH^-]$ = 20×10^{-2} mol dm^{-3}

[Tetraethylene glycol] = 2.0×10^{-2} mol dm^{-3}

[Ru(VI)] = 6.55×10^{-6} mol dm^{-3}

μ = 0.20 mole dm^{-3}

Time min	$Ce(SO_4)_2$ 1.00×10^{-3}M in ml.	$k_0\times10^2$ ml min^{-1}
1	0.30	
5	0.48	4.5
10	0.70	4.4
20	1.16	4.6
30	1.60	4.4
40	2.02	4.2
50	2.44	4.2
60	2.84	4.0
70	3.24	4.0
80	3.64	4.0
90	4.04	4.0
T_∞	10.00	

Average $k_0 = 4.27\times10^{-2}$ ml min^{-1}

A.D. = ± 4.77%

$k_s = 8.54\times10^{-6}$ mol dm^{-3} min^{-1}

$\left(-\frac{dc}{dt}\right) = 8.94\times10^{-6}$ mole dm^{-3} min^{-1}

Table 3.114

Temp. = 35°C

$[K_3Fe(CN)_6]$ = 2.00×10^{-3} mol dm^{-3}

$[OH^-]$ = 15×10^{-2} mol dm^{-3}

[Tetraethylene glycol] = 2.0×10^{-2} mol dm^{-3}

[Ru(VI)] = 6.55×10^{-6} mol dm^{-3}

μ = 0.20 mole dm^{-3}

Time min	$Ce(SO_4)_2$ 1.00×10^{-3}M in ml.	$k_0\times10^2$ ml min^{-1}
1	0.34	
5	0.56	5.5
10	0.84	5.6
15	1.12	5.6
20	1.42	6.0
25	1.70	5.6
30	1.96	5.2
35	2.22	5.2
40	2.50	5.6
45	2.76	5.2
50	3.04	5.6
T_∞	10.00	

Average $k_0 = 5.51\times10^{-2}$ ml min^{-1}

A.D. = ± 3.41%

$k_s = 11.02\times10^{-6}$ mol dm^{-3} min^{-1}

$\left(-\frac{dc}{dt}\right) = 11.20\times10^{-6}$ mole dm^{-3} min^{-1}

Table 3.115

Temp. = 35°C

$[K_3Fe(CN)_6]$ = 2.00×10^{-3} mol dm^{-3}

$[OH^-]$ = 10×10^{-2} mol dm^{-3}

[Tetraethylene glycol] = 2.0×10^{-2} mol dm^{-3}

[Ru(VI)] = 6.55×10^{-6} mol dm^{-3}

μ = 0.20 mole dm^{-3}

Time min	$Ce(SO_4)_2$ 1.00×10^{-3}M in ml.	$k_0\times10^2$ ml min^{-1}
1	0.38	
5	0.74	9.0
10	1.20	9.2
15	1.68	9.6
20	2.14	9.2
25	2.60	9.2
30	3.06	9.2
35	3.50	8.8
40	3.96	9.2
45	4.40	8.8
50	4.84	8.8
T_∞	10.00	

Average $k_0 = 9.1\times10^{-2}$ ml min^{-1}

A.D. = ± 2.19%

$k_s = 18.2\times10^{-6}$ mol dm^{-3} min^{-1}

$\left(-\frac{dc}{dt}\right) = 18.26\times10^{-6}$ mole dm^{-3} min^{-1}

Table 3.116

Temp. = 35°C

$[K_3Fe(CN)_6]$ = 2.00×10^{-3} mol dm^{-3}

$[OH^-]$ = 6.25×10^{-2} mol dm^{-3}

[Tetraethylene glycol] = 2.0×10^{-2} mol dm^{-3}

[Ru(VI)] = 6.55×10^{-6} mol dm^{-3}

μ = 0.20 mole dm^{-3}

Time min	$Ce(SO_4)_2$ 1.00×10^{-3}M in ml.	$k_0\times10^2$ ml min^{-1}
1	0.42	
5	0.92	12.5
10	1.56	12.8
15	2.20	12.8
20	2.82	12.4
25	3.44	12.4
30	4.06	12.4
35	4.70	12.8
40	5.32	12.4
45	5.94	12.4
50	6.54	12.0
T_∞	10.00	

Average $k_0 = 12.49\times10^{-2}$ ml min^{-1}

A.D. = ± 1.50%

$k_s = 24.98\times10^{-6}$ mol dm^{-3} min^{-1}

$\left(-\frac{dc}{dt}\right) = 25.02\times10^{-6}$ mole dm^{-3} min^{-1}

Table 3.117

Temp. = 35°C

$[K_3Fe(CN)_6]$ = 2.00×10^{-3} mol dm^{-3}

$[OH^-]$ = 5.00×10^{-2} mol dm^{-3}

[Tetraethylene glycol] = 2.0×10^{-2} mol dm^{-3}

[Ru(VI)] = 6.55×10^{-6} mol dm^{-3}

μ = 0.20 mole dm^{-3}

Time min	$Ce(SO_4)_2$ 1.00×10^{-3}M in ml.	$k_0\times10^2$ ml min^{-1}
1	0.46	
3	0.76	15.0
6	1.20	14.6
9	1.66	15.3
12	2.10	14.6
15	2.54	14.6
18	2.96	14.0
21	3.38	14.0
24	3.80	14.0
27	4.24	14.6
30	4.68	14.6
T_∞	10.00	

Average $k_0 = 14.53\times10^{-2}$ ml min^{-1}

A.D. = ± 2.18%

$k_s = 29\times10^{-6}$ mol dm^{-3} min^{-1}

$\left(-\frac{dc}{dt}\right) = 29.42\times10^{-6}$ mole dm^{-3} min^{-1}

Table 3.118

Temp. = 35°C

$[K_3Fe(CN)_6]$ = 2.00×10^{-3} mol dm^{-3}

$[OH^-]$ = 2.0×10^{-2} mol dm^{-3}

[Tetraethylene glycol] = 2.0×10^{-2} mol dm^{-3}

[Ru(VI)] = 6.55×10^{-6} mol dm^{-3}

μ = 0.20 mole dm^{-3}

Time min	$Ce(SO_4)_2$ 1.00×10^{-3}M in ml.	$k_0\times10^2$ ml min^{-1}
1	0.50	
3	0.90	20.0
6	1.50	20.0
9	2.12	20.6
12	2.74	20.6
15	3.38	20.8
18	4.00	20.6
21	4.60	20.0
24	5.18	19.3
27	5.76	19.3
30	6.34	19.3
T_∞	10.00	

Average $k_0 = 20.05\times10^{-2}$ ml min^{-1}

A.D. = ± 2.39%

$k_s = 40.01\times10^{-6}$ mol dm^{-3} min^{-1}

$\left(-\frac{dc}{dt}\right) = 40.34\times10^{-6}$ mole dm^{-3} min^{-1}

Table 3.119

Temp. = 35°C
$[K_3Fe(CN)_6]$ = 2.00×10^{-3} mol dm^{-3}
[Tetraethylene glycol] = 2.00×10^{-2} mol dm^{-3}
[Ru(VI)] = 6.55×10^{-6} mol dm^{-3}
μ = 0.20 mol dm^{-3}

$[OH^-]\times10^2$ mol dm^{-3}	$k_s\times10^6$ mol dm^{-3} min^{-1}	$\left(-\frac{dc}{dt}\right)\times10^6$ mol dm^{-3} min^{-1}
20.00	8.54	8.94
15.10	11.02	11.20
10.00	18.20	18.26
6.25	24.98	25.02
5.00	29.06	29.42
2.00	40.01	40.34

Table 3.120

Temp. = 35°C
$[K_3Fe(CN)_6]$ = 2.00×10^{-3} mol dm^{-3}
[Tetraethylene glycol] = 4.00×10^{-2} mol dm^{-3}
[Ru(VI)] = 6.55×10^{-6} mol dm^{-3}
μ = 0.20 mol dm^{-3}

$[OH^-]\times10^2$ mol dm^{-3}	$k_s\times10^6$ mol dm^{-3} min^{-1}	$\left(-\frac{dc}{dt}\right)\times10^6$ mol dm^{-3} min^{-1}
20.00	21.54	21.16
15.10	25.52	25.45
10.00	32.56	32.64
6.25	40.05	40.00
5.00	45.08	45.18
2.00	59.60	59.98

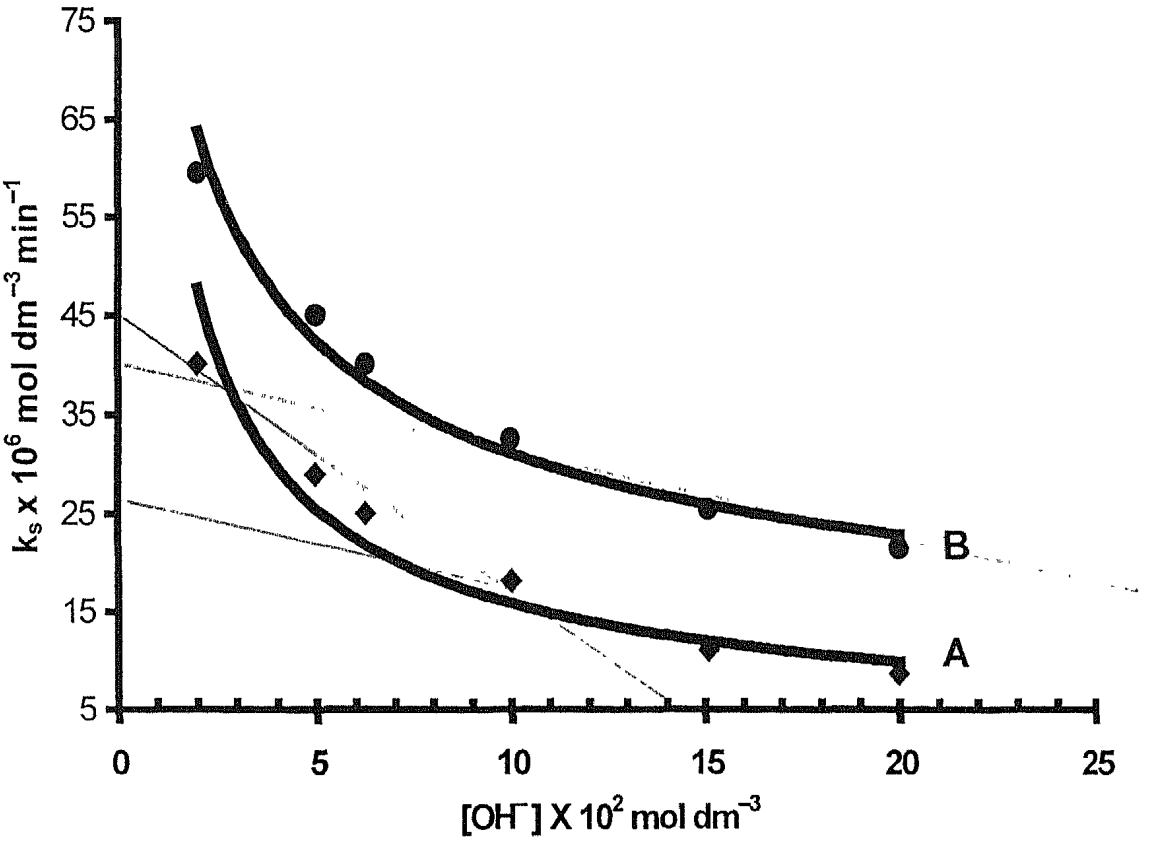


Figure 3.15 **$[K_3Fe(CN)_6] = 2.00 \times 10^{-3}$ mol dm^{-3}; [Ru(VI)] = 6.55×10^{-6} mol dm^{-3} ; [Tetraethylene Glycol] (A) = 2.00×10^{-2} mol dm^{-3} (B) = 4.0×10^{-2} mol dm^{-3}; μ = 0.20 mol dm^{-3}, Temp.= 35°C.;**

3.4 DETERMINATION OF ORDER OF THE REACTION WITH RESPECT TO ORGANIC SUBSTRATE

The effect of variation of substrate concentration on the reaction velocity has been given in this section.

The first series of experiments have been performed with 4-methyl pentanol-2. The experiments have been performed by keeping the concentration of other reactants constant and changing the concentration of 4-methyl pentanol-2. The result thus obtained are given in tables (3.121 to 3.126).

The first column of the table represents interval of time in minutes, second column represents the amount of hexacyanoferrate(II) produced at different intervals of time in terms of volume of cerium sulphate and the third column represents the observed zero order rate constant. i.e. $k_0 = \Delta x / \Delta t$, where Δx is the volume in ml of cerium sulphate solution consumed for 5ml of reaction mixture which is equivalent to hexacyanoferrate(II) produced in time Δt minutes. The average value of k_0, the standard zero order rate constant (k_s) and the value of (–dc/dt) are given below each table. The summarised results are given in tables (3.127).

These results have been reproduced in the form of graphs (fig. 3.16(A)). These graphs clearly indicate that the velocity of reaction is directly proportional to substrate concentration in the lower range of substrate concentration but at higher concentration of substrate deviation occurs and ultimately reaction velocity tends to attain a constant value. After a certain range of concentration of substrate the reaction becomes too fast to

study. The details will be discussed in the last chapter.

Similar experiments have also been performed to study the effect of variation of concentration of 4-methyl pentanol-2 at different concentrations, of the other reactants keeping the ionic strength constant and results thus obtained are given in the summarised table (3.128) and also reproduced in the form of graph (fig. 3.16(B)).

Table 3.121

Temp. = 35°C

$[K_3Fe(CN)_6]$ = 2.00×10^{-3} mol dm^{-3}

$[OH^-]$ = 10×10^{-2} mol dm^{-3}

[4-methyl pentanol-2] = 7.9×10^{-3} mol dm^{-3}

[Ru(VI)] = 2.18×10^{-6} mol dm^{-3}

μ = 0.25 mole dm^{-3}

Time min	$Ce(SO_4)_2$ 1.25×10^{-3}M in ml.	$k_0\times10^2$ ml min^{-1}
1	0.60	
5	0.70	2.5
10	0.82	2.4
20	1.04	2.2
30	1.26	2.2
40	1.50	2.4
50	1.70	2.0
60	1.90	2.0
70	2.12	2.2
80	2.34	2.2
90	2.54	2.0
T_∞	8.00	

Average $k_0 = 2.21\times10^{-2}$ ml min^{-1}

A.D. = ± 4.06%

$k_s = 5.52\times10^{-6}$ mol dm^{-3} min^{-1}

$\left(-\frac{dc}{dt}\right) = 5.68\times10^{-6}$ mole dm^{-3} min^{-1}

Table 3.122

Temp. = 35°C

$[K_3Fe(CN)_6]$ = 2.00×10^{-3} mol dm^{-3}

$[OH^-]$ = 10×10^{-2} mol dm^{-3}

[4-methyl pentanol-2] = 15.8×10^{-3} mol dm^{-3}

[Ru(VI)] = 2.18×10^{-6} mol dm^{-3}

μ = 0.25 mole dm^{-3}

Time min	$Ce(SO_4)_2$ 1.25×10^{-3}M in ml.	$k_0\times10^2$ ml min^{-1}
1	0.68	
5	0.88	5.0*
10	1.10	4.4
20	1.52	4.2
30	1.92	4.0
40	2.32	4.0
50	2.70	3.8
60	3.08	3.8
70	3.46	3.8
80	3.84	3.8
90	4.20	3.6
T_∞	8.00	

Average $k_0 = 3.9\times10^{-2}$ ml min^{-1}

A.D. = ± 4.61%

$k_s = 9.75\times10^{-6}$ mol dm^{-3} min^{-1}

$\left(-\frac{dc}{dt}\right) = 9.76\times10^{-6}$ mole dm^{-3} min^{-1}

Table 3.123

Temp. = 35°C

$[K_3Fe(CN)_6]$ = 2.00×10^{-3} mol dm^{-3}

$[OH^-]$ = 10×10^{-2} mol dm^{-3}

[4-methyl pentanol-2] = 3.16×10^{-2} mol dm^{-3}

[Ru(VI)] = 2.18×10^{-6} mol dm^{-3}

μ = 0.25 mole dm^{-3}

Time min	$Ce(SO_4)_2$ 1.25×10^{-3}M in ml.	$k_0\times10^2$ ml min^{-1}
1	0.70	
5	1.0	7.5
10	1.42	8.4
15	1.82	8.0
20	2.22	8.0
30	3.00	7.8
40	3.86	8.6
50	4.66	8.0
60	5.40	7.4
70	6.00	6.0*
T_∞	8.00	

Average $k_0 = 7.96\times10^{-2}$ ml min^{-1}

A.D. = ± 3.64%

$k_s = 19.9\times10^{-6}$ mol dm^{-3} min^{-1}

$\left(-\frac{dc}{dt}\right) = 19.68\times10^{-6}$ mole dm^{-3} min^{-1}

Table 3.124

Temp. = 35°C

$[K_3Fe(CN)_6]$ = 2.00×10^{-3} mol dm^{-3}

$[OH^-]$ = 10×10^{-2} mol dm^{-3}

[4-methyl pentanol-2] = 4.74×10^{-2} mol dm^{-3}

[Ru(VI)] = 2.18×10^{-6} mol dm^{-3}

μ = 0.25 mole dm^{-3}

Time min	$Ce(SO_4)_2$ 1.25×10^{-3}M in ml.	$k_0\times10^2$ ml min^{-1}
1	0.84	
3	1.10	13.0
6	1.50	13.3
9	1.90	13.3
12	2.28	12.6
15	2.66	12.6
20	3.28	12.4
25	3.88	12.0
30	4.52	12.8
40	5.72	12.0
50	6.20	4.8*
T_∞	8.00	

Average $k_0 = 12.6\times10^{-2}$ ml min^{-1}

A.D. = ± 2.93%

$k_s = 31.5\times10^{-6}$ mol dm^{-3} min^{-1}

$\left(-\frac{dc}{dt}\right) = 31.78\times10^{-6}$ mole dm^{-3} min^{-1}

Table 3.125

Temp. = 35°C

$[K_3Fe(CN)_6]$ = 2.00×10^{-3} mol dm^{-3}

$[OH^-]$ = 10×10^{-2} mol dm^{-3}

[4-methyl pentanol-2] = 6.32×10^{-2} mol dm^{-3}

[Ru(VI)] = 2.18×10^{-6} mol dm^{-3}

μ = 0.25 mole dm^{-3}

Time min	$Ce(SO_4)_2$ 1.25×10^{-3}M in ml.	$k_0\times10^2$ ml min^{-1}
1	0.88	
3	1.20	16.0
6	1.70	16.6
9	2.18	16.0
12	2.66	16.0
15	3.16	16.6
18	3.64	16.0
21	4.14	16.6
24	4.64	16.6
27	5.12	16.0
30	5.60	16.0
35	6.20	12.0*
T_∞	8.00	

Average $k_0 = 16.24\times10^{-2}$ ml min^{-1}

A.D. = ± 1.77%

$k_s = 40.60\times10^{-6}$ mol dm^{-3} min^{-1}

$\left(-\frac{dc}{dt}\right) = 40.22\times10^{-6}$ mole dm^{-3} min^{-1}

Table 3.126

Temp. = 35°C

$[K_3Fe(CN)_6]$ = 2.00×10^{-3} mol dm^{-3}

$[OH^-]$ = 10×10^{-2} mol dm^{-3}

[4-methyl pentanol-2] = 7.9×10^{-2} mol dm^{-3}

[Ru(VI)] = 2.18×10^{-6} mol dm^{-3}

μ = 0.25 mole dm^{-3}

Time min	$Ce(SO_4)_2$ 1.25×10^{-3}M in ml.	$k_0\times10^2$ ml min^{-1}
1	0.94	
2	1.16	22.0
4	1.56	20.0
6	2.00	22.0
8	2.42	21.0
10	2.84	21.0
12	3.26	21.0
15	3.86	20.0
18	4.48	20.6
21	5.10	20.6
24	5.68	19.3
27	6.10	14.0*
T_∞	8.00	

Average $k_0 = 20.75\times10^{-2}$ ml min^{-1}

A.D. = ± 3.37%

$k_s = 51.87\times10^{-6}$ mol dm^{-3} min^{-1}

$\left(-\frac{dc}{dt}\right) = 52.00\times10^{-6}$ mole dm^{-3} min^{-1}

Table 3.127

Temp. = 35°C
$[K_3Fe(CN)_6]$ = 2.00×10^{-3} mol dm^{-3}
$[OH^-]$ = 10×10^{-2} mol dm^{-3}
[Ru(VI)] = 2.18×10^{-6} mol dm^{-3}
μ = 0.25 mol dm^{-3}

[4-methyl pentanol-2]$\times10^2$ mol dm^{-3}	$k_s\times10^6$ mol dm^{-3} min^{-1}	$\left(-\frac{dc}{dt}\right)\times10^6$ mol dm^{-3} min^{-1}	$\frac{k_s}{[4-\text{methyl pen tan ol}-2]}\times10^4$ min^{-1}
7.90	51.87	52.00	6.55
6.32	40.60	40.22	6.42
4.74	31.50	31.78	6.64
3.16	19.90	19.68	6.29
1.58	9.75	9.76	6.17
0.79	5.52	5.68	6.98

Table 3.128

Temp. = 35°C
$[K_3Fe(CN)_6]$ = 2.00×10^{-3} mol dm^{-3}
$[OH^-]$ = 5.0×10^{-2} mol dm^{-3}
[Ru(VI)] = 2.18×10^{-6} mol dm^{-3}
μ = 0.25mol dm^{-3}

[4-methyl pentanol-2]$\times10^2$ mol dm^{-3}	$k_s\times10^6$ mol dm^{-3} min^{-1}	$\left(-\frac{dc}{dt}\right)\times10^6$ mol dm^{-3} min^{-1}	$\frac{k_s}{[4-\text{methyl pen tan ol}-2]}\times10^4$ min^{-1}
7.90	62.0	62.28	7.84
6.32	52.87	52.20	8.36
4.74	42.32	42.67	8.92
3.16	32.92	33.02	10.41
1.58	15.50	15.80	9.81
0.79	7.40	7.98	9.36

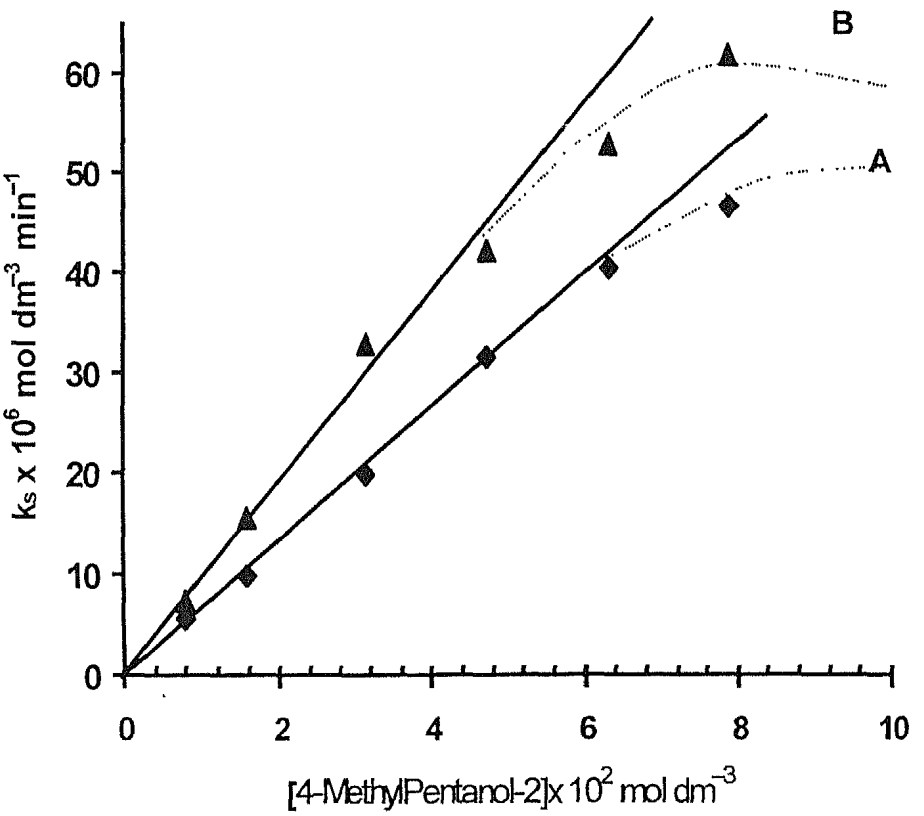


Figure 3.16

Temp.= 35°C; $[K_3Fe(CN)_6] = 2.00 \times 10^{-3}$ mol dm^{-3}; $[OH^-]$= (A) = 10.00×10^{-2} mol dm^{-3}(B) = 5.00×10^{-2} mol dm^{-3}; [Ru(VI)]= 2.18×10^{-6} mol dm^{-3}; μ = 0.25 mol dm^{-3};

The second series of experiments have been performed with 2-methoxy ethanol. The experiments have been performed by keeping the concentration of other reactant constant and varying the concentration of 2-methoxy ethanol. The results thus obtained are presented in tables (3.129 to 3.134).

The first, second and third column of the above table represents interval of time in minutes, the amount of hexacyanoferrate(II) produced at different intervals of time in terms of volume of ceric sulphate and the observed zero order rate constant, i.e. $k_0 = \Delta x/\Delta t$ respectively. Where Δx is the volume in ml of cerium sulphate solution consumed for 5 ml of reaction mixture which is equivalent to hexacyanoferrate(II) produced in time Δt minutes. The average value of k_0, the standard zero order rate constant (k_s) and the value of ($-dc/dt$) are given below each table. The summarised results are given in tables (3.135 and 3.136). These results have been reproduced in the form graphs (Fig. 3.17(A) and 3.17(B)) and these graphs clearly indicates that the velocity of reaction is directly proportional to substrate concentration in the lower range of substrate concentration but at higher concentration of substrate deviation occurs and ultimately reaction velocity tends to attain a constant value. The details will be discussed in the last chapter.

Table 3.129

Temp. = 35°C

$[K_3Fe(CN)_6]$ = 2.00×10^{-3} mol dm^{-3}

$[OH^-]$ = 10×10^{-2} mol dm^{-3}

[2-methoxy ethanol] = 10×10^{-2} mol dm^{-3}

[Ru(VI)] = 15.5×10^{-7} mol dm^{-3}

μ = 0.20 mole dm^{-3}

Time min	$Ce(SO_4)_2$ 1.00×10^{-3}M in ml.	$k_0\times10^2$ ml min^{-1}
1	0.86	
2	1.22	36.0
4	1.92	35.0
6	2.62	35.0
8	3.34	36.0
10	4.04	35.0
12	4.74	35.0
14	5.42	34.0
16	6.10	34.0
18	6.78	34.0
20	7.18	20.0*
T_∞	10.00	

Average $k_0 = 35.0\times10^{-2}$ ml min^{-1}

A.D. = ± 1.57%

$k_s = 70.0\times10^{-6}$ mol dm^{-3} min^{-1}

$\left(-\frac{dc}{dt}\right) = 70.12\times10^{-6}$ mole dm^{-3} min^{-1}

Table 3.130

Temp. = 35°C

$[K_3Fe(CN)_6]$ = 2.00×10^{-3} mol dm^{-3}

$[OH^-]$ = 10×10^{-2} mol dm^{-3}

[2-methoxy ethanol] = 5.00×10^{-2} mol dm^{-3}

[Ru(VI)] = 15.5×10^{-7} mol dm^{-3}

μ = 0.20 mole dm^{-3}

Time min	$Ce(SO_4)_2$ 1.00×10^{-3}M in ml.	$k_0\times10^2$ ml min^{-1}
1	0.80	
3	1.20	20.0
6	1.82	20.6
9	2.44	20.6
12	3.04	20.0
15	3.64	20.0
18	4.24	20.0
21	4.82	19.3
24	5.40	19.3
27	5.98	19.3
30	6.56	19.3
T_∞	10.00	

Average $k_0 = 19.8\times10^{-2}$ ml min^{-1}

A.D. = ± 2.22%

$k_s = 39.60\times10^{-6}$ mol dm^{-3} min^{-1}

$\left(-\frac{dc}{dt}\right) = 39.00\times10^{-6}$ mole dm^{-3} min^{-1}

Table 3.131

Temp. = 35°C
$[K_3Fe(CN)_6]$ = 2.00×10^{-3} mol dm^{-3}
$[OH^-]$ = 10×10^{-2} mol dm^{-3}
[2-methoxy ethanol] = 3.33×10^{-2} mol dm^{-3}
[Ru(VI)] = 15.5×10^{-7} mol dm^{-3}
μ = 0.20 mole dm^{-3}

Time min	$Ce(SO_4)_2$ 1.00×10^{-3}M in ml.	$k_0\times10^2$ ml min^{-1}
1	0.78	
5	1.32	13.5
10	2.00	13.6
15	2.66	13.2
20	3.32	13.2
25	3.96	12.8
30	4.62	13.2
35	5.26	12.8
40	5.92	13.2
45	6.56	12.8
50	7.06	10.0*
T_∞	10.00	

Average $k_0 = 13.10\times10^{-2}$ ml min^{-1}
A.D. = ± 1.83%
$k_s = 26.20\times10^{-6}$ mol dm^{-3} min^{-1}
$\left(-\frac{dc}{dt}\right) = 26.22\times10^{-6}$ mole dm^{-3} min^{-1}

Table 3.132

Temp. = 35°C
$[K_3Fe(CN)_6]$ = 2.00×10^{-3} mol dm^{-3}
$[OH^-]$ = 10×10^{-2} mol dm^{-3}
[2-methoxy ethanol] = 2.50×10^{-2} mol dm^{-3}
[Ru(VI)] = 15.5×10^{-7} mol dm^{-3}
μ = 0.20 mole dm^{-3}

Time min	$Ce(SO_4)_2$ 1.00×10^{-3}M in ml.	$k_0\times10^2$ ml min^{-1}
1	0.74	
5	1.18	11.0
10	1.72	10.8
15	2.26	10.8
20	2.80	10.8
25	3.36	11.2
30	3.90	10.8
35	4.44	10.8
40	4.96	10.4
45	5.48	10.4
50	6.00	10.4
T_∞	10.00	

Average $k_0 = 10.74\times10^{-2}$ ml min^{-1}
A.D. = ± 1.89%
$k_s = 21.40\times10^{-6}$ mol dm^{-3} min^{-1}
$\left(-\frac{dc}{dt}\right) = 21.47\times10^{-6}$ mole dm^{-3} min^{-1}

Table 3.133

Temp. = 35°C

$[K_3Fe(CN)_6]$ = 2.00×10^{-3} mol dm^{-3}

$[OH^-]$ = 10×10^{-2} mol dm^{-3}

[2-methoxy ethanol] = 2.00×10^{-2} mol dm^{-3}

[Ru(VI)] = 15.5×10^{-7} mol dm^{-3}

μ = 0.20 mole dm^{-3}

Time min	$Ce(SO_4)_2$ 1.00×10^{-3}M in ml.	$k_0\times10^2$ ml min^{-1}
1	0.62	
5	0.98	9.0
10	1.42	8.8
15	1.84	8.4
20	2.26	8.4
25	2.66	8.0
30	3.06	8.0
35	3.46	8.0
40	3.88	8.4
45	4.28	8.0
50	4.68	8.0
T_∞	10.00	

Average $k_0 = 8.3\times10^{-2}$ ml min^{-1}

A.D. = ± 3.61%

$k_s = 16.60\times10^{-6}$ mol dm^{-3} min^{-1}

$\left(-\frac{dc}{dt}\right) = 16.66\times10^{-6}$ mole dm^{-3} min^{-1}

Table 3.134

Temp. = 35°C

$[K_3Fe(CN)_6]$ = 2.00×10^{-3} mol dm^{-3}

$[OH^-]$ = 10×10^{-2} mol dm^{-3}

[2-methoxy ethanol] = 1.25×10^{-2} mol dm^{-3}

[Ru(VI)] = 15.5×10^{-7} mol dm^{-3}

μ = 0.20 mole dm^{-3}

Time min	$Ce(SO_4)_2$ 1.00×10^{-3}M in ml.	$k_0\times10^2$ ml min^{-1}
1	0.60	
5	0.84	6.0
10	1.12	5.6
20	1.62	5.0
30	2.12	5.0
40	2.74	5.2
50	3.24	5.0
60	3.74	5.0
70	4.24	5.0
80	4.74	5.0
90	5.26	5.0
T_∞	10.00	

Average $k_0 = 5.2\times10^{-2}$ ml min^{-1}

A.D. = ± 4.61%

$k_s = 10.40\times10^{-6}$ mol dm^{-3} min^{-1}

$\left(-\frac{dc}{dt}\right) = 10.54\times10^{-6}$ mole dm^{-3} min^{-1}

Table 3.135

Temp. = 35°C
$[K_3Fe(CN)_6]$ = 2.00×10^{-3} mol dm^{-3}
$[OH^-]$ = 10×10^{-2} mol dm^{-3}
[Ru(VI)] = 15.5×10^{-7} mol dm^{-3}
μ = 0.20 mol dm^{-3}

[2-methoxy ethanol]$\times10^2$ mol dm^{-3}	$k_s\times10^6$ mol dm^{-3} min^{-1}	$\left(-\frac{dc}{dt}\right)\times10^6$ mol dm^{-3} min^{-1}	$\frac{k_s}{[2-\text{methoxy ethanol}]}$ $\times10^4$ min^{-1}
10.00	70.00	70.12	7.00
5.00	39.60	39.00	7.92
3.33	26.20	26.22	7.93
2.50	21.40	21.47	8.56
2.00	16.60	16.66	8.30
1.25	10.40	10.54	8.32

Table 3.136

Temp. = 35°C
$[K_3Fe(CN)_6]$ = 2.00×10^{-3} mol dm^{-3}
$[OH^-]$ = 5.0×10^{-2} mol dm^{-3}
[Ru(VI)] = 15.5×10^{-7} mol dm^{-3}
μ = 0.20 mol dm^{-3}

[2-methoxy-ethanol]$\times10^2$ mol dm^{-3}	$k_s\times10^6$ mol dm^{-3} min^{-1}	$\left(-\frac{dc}{dt}\right)\times10^6$ mol dm^{-3} min^{-1}	$\frac{k_s}{[2-\text{methoxy ethanol}]}$ $\times10^4$ min^{-1}
10.00	99.00	99.18	9.90
5.00	54.80	54.90	10.96
3.33	36.16	36.00	10.95
2.50	28.00	27.95	11.20
2.00	21.90	21.84	10.95
1.25	13.36	13.24	10.68

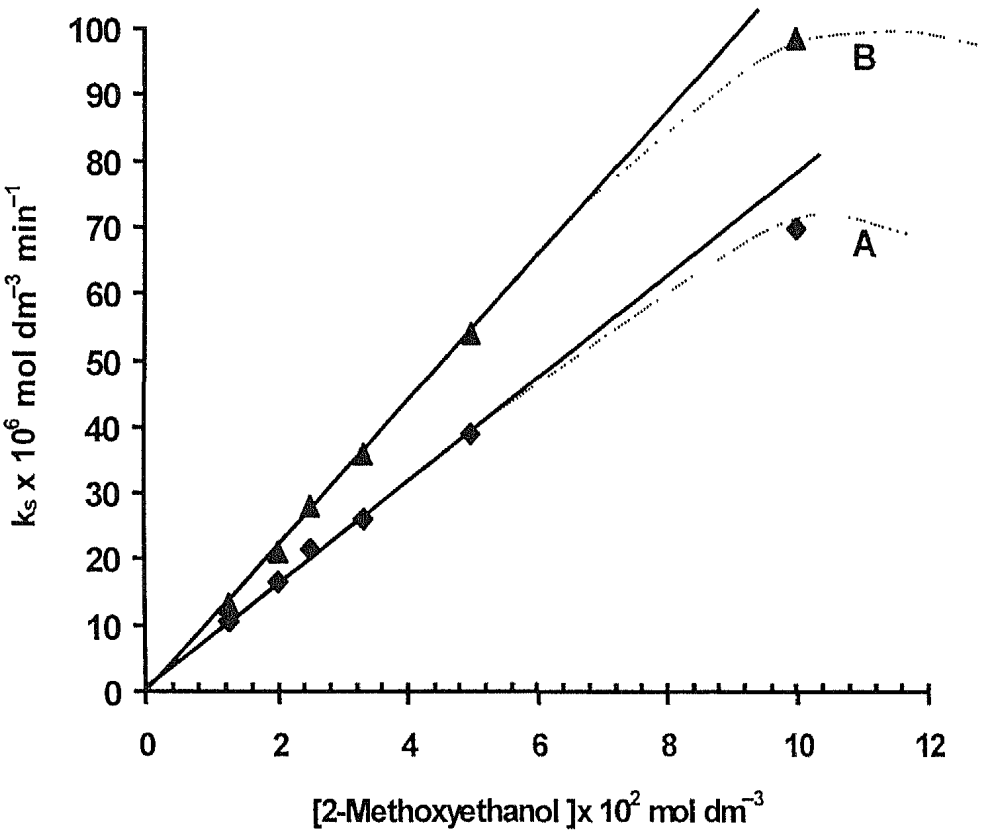


Figure 3.17

Temp.= 35°C; $[K_3Fe(CN)_6] = 2.00 \times 10^{-3}$ mol dm^{-3}; $[OH^-]$= (A) = 10.00×10^{-2} mol dm^{-3}(B) = 5.00×10^{-2} mol dm^{-3}; [Ru(VI)]= 15.5×10^{-7} mol dm^{-3}; $\mu = 0.20$ mol dm^{-3};

The third series of experiments have been performed with Diethylene glycol. The observation have been made by keeping the concentration of other reactants constant and varying the concentration of diethylene glycol. The results thus obtained are given in the tables (3.137 to 3.142). The standard zero order rate constants have been calculated in the same way as in the proceeding section and are given below in each table. Here also the value of (dc/dt) initial velocity has been calculated by plotting a graph between time Vs. remaining concentration of hexacyanoferrate(II) and values thus obtained are given below in each table.

The summarised results are given in the tables (3.143 and 3.144). These tables clearly indicate that reaction velocity increases with increase in substrate concentration. These results are given in summarised tables (3.143 and 3.144) are reproduced in the form of graphs (fig. 3.18(A) and 3.18(B)). These graphs clearly indicate that the velocity of the reaction is directly proportional to the substrate concentration in the lower range of diethylene glycol concentration but at higher concentration deviation occurs.

Table 3.137

Temp. = 30°C

$[K_3Fe(CN)_6]$ = 2.00×10^{-3} mol dm^{-3}

$[OH^-]$ = 2.00×10^{-1} mol dm^{-3}

[Diethylene glycol] = 2.00×10^{-1} mol dm^{-3}

[Ru(VI)] = 3.66×10^{-6} mol dm^{-3}

μ = 0.25 mole dm^{-3}

Time min	$Ce(SO_4)_2$ 1.00×10^{-3}M in ml.	$k_0\times10^2$ ml min^{-1}
1	1.52	
3	2.68	58.0*
5	3.60	46.0*
6	3.98	38.0
7	4.38	40.0
8	4.74	36.0
9	5.12	38.0
10	5.48	36.0
11	5.86	38.0
12	6.20	34.0
13	6.58	38.0
14	6.94	36.0
15	7.20	26.0*
T_∞	10.00	

Average $k_0 = 39.3\times10^{-2}$ ml min^{-1}

A.D. = ± 5.95%

$k_s = 78.6\times10^{-6}$ mol dm^{-3} min^{-1}

$\left(-\frac{dc}{dt}\right) = 78.82\times10^{-6}$ mole dm^{-3} min^{-1}

Table 3.138

Temp. = 30°C

$[K_3Fe(CN)_6]$ = 2.00×10^{-3} mol dm^{-3}

$[OH^-]$ = 2.00×10^{-1} mol dm^{-3}

[Diethylene glycol] = 1.00×10^{-1} mol dm^{-3}

[Ru(VI)] = 3.66×10^{-6} mol dm^{-3}

μ = 0.25 mole dm^{-3}

Time min	$Ce(SO_4)_2$ 1.00×10^{-3}M in ml.	$k_0\times10^2$ ml min^{-1}
1	0.86	
3	1.34	24.0
5	1.84	25.0
7	2.30	23.0
9	2.78	24.0
11	3.18	20.0
13	3.60	21.0
15	4.10	25.0
17	4.50	20.0
19	4.92	21.0
21	5.32	20.0
T_∞	10.00	

Average $k_0 = 22.3\times10^{-2}$ ml min^{-1}

A.D. = ± 5.52%

$k_s = 44.6\times10^{-6}$ mol dm^{-3} min^{-1}

$\left(-\frac{dc}{dt}\right) = 43.96\times10^{-6}$ mole dm^{-3} min^{-1}

Table 3.139

Temp. = 30°C
$[K_3Fe(CN)_6]$ = 2.00×10^{-3} mol dm^{-3}
$[OH^-]$ = 2.00×10^{-1} mol dm^{-3}
[Diethylene glycol] = 6.25×10^{-2} mol dm^{-3}
[Ru(VI)] = 3.66×10^{-6} mol dm^{-3}
μ = 0.25 mole dm^{-3}

Time min	$Ce(SO_4)_2$ 1.00×10^{-3}M in ml.	$k_0\times10^2$ ml min^{-1}
1	0.58	
4	1.08	16.6
7	1.50	14.0
10	1.92	14.0
13	2.34	14.0
16	2.76	14.0
19	3.18	14.0
21	3.50	16.0
24	3.86	12.0
27	4.28	14.0
30	4.68	13.3
T_∞	10.00	

Average $k_0 = 14.19\times10^{-2}$ ml min^{-1}
A.D. = ± 5.37%
$k_s = 28.38\times10^{-6}$ mol dm^{-3} min^{-1}
$\left(-\frac{dc}{dt}\right) = 28.64\times10^{-6}$ mole dm^{-3} min^{-1}

Table 3.140

Temp. = 30°C
$[K_3Fe(CN)_6]$ = 2.00×10^{-3} mol dm^{-3}
$[OH^-]$ = 2.00×10^{-1} mol dm^{-3}
[Diethylene glycol] = 5.00×10^{-2} mol dm^{-3}
[Ru(VI)] = 3.66×10^{-6} mol dm^{-3}
μ = 0.25 mole dm^{-3}

Time min	$Ce(SO_4)_2$ 1.00×10^{-3}M in ml.	$k_0\times10^2$ ml min^{-1}
1	0.46	
4	0.94	16.0*
8	1.44	12.5
12	1.80	9.0
16	2.30	12.5
20	2.78	12.0
24	3.26	12.0
28	3.76	12.5
32	4.24	12.0
36	4.62	9.5
40	5.10	12.0
T_∞	10.00	

Average $k_0 = 12.0\times10^{-2}$ ml min^{-1}
A.D. = ± 5.87%
$k_s = 24.0\times10^{-6}$ mol dm^{-3} min^{-1}
$\left(-\frac{dc}{dt}\right) = 24.22\times10^{-6}$ mole dm^{-3} min^{-1}

Table 3.141

Temp. = 30°C
$[K_3Fe(CN)_6]$ = 2.00×10^{-3} mol dm^{-3}
$[OH^-]$ = 2.00×10^{-1} mol dm^{-3}
[Diethylene glycol] = 2.50×10^{-2} mol dm^{-3}
[Ru(VI)] = 3.66×10^{-6} mol dm^{-3}
μ = 0.25 mole dm^{-3}

Time min	$Ce(SO_4)_2$ 1.00×10^{-3}M in ml.	$k_0\times10^2$ ml min^{-1}
1	0.28	
5	0.62	8.5
10	0.88	5.2
15	1.18	6.0
20	1.50	6.4
30	2.14	6.4
40	2.78	6.4
50	3.42	6.4
60	4.10	6.8
70	4.86	7.6
80	5.56	7.0
T_∞	10.00	

Average $k_0 = 6.71\times10^{-2}$ ml min^{-1}
A.D. = ± 5.71%
$k_s = 13.70\times10^{-6}$ mol dm^{-3} min^{-1}
$\left(-\frac{dc}{dt}\right) = 13.14\times10^{-6}$ mole dm^{-3} min^{-1}

Table 3.142

Temp. = 30°C
$[K_3Fe(CN)_6]$ = 2.00×10^{-3} mol dm^{-3}
$[OH^-]$ = 2.00×10^{-1} mol dm^{-3}
[Diethylene glycol] = 2.00×10^{-2} mol dm^{-3}
[Ru(VI)] = 3.66×10^{-6} mol dm^{-3}
μ = 0.25 mole dm^{-3}

Time min	$Ce(SO_4)_2$ 1.00×10^{-3}M in ml.	$k_0\times10^2$ ml min^{-1}
1	0.26	
6	0.52	5.2
14	0.96	5.5
24	1.46	5.0
34	1.96	5.0
44	2.48	5.2
54	3.00	5.2
64	3.52	5.2
74	4.04	5.2
84	4.56	5.2
94	5.08	5.2
T_∞	10.00	

Average $k_0 = 5.12\times10^{-2}$ ml min^{-1}
A.D. = ± 2.30%
$k_s = 10.24\times10^{-6}$ mol dm^{-3} min^{-1}
$\left(-\frac{dc}{dt}\right) = 9.98\times10^{-6}$ mole dm^{-3} min^{-1}

Table 3.143

Temp. = 30°C
$[K_3Fe(CN)_6]$ = 2.00×10^{-3} mol dm^{-3}
$[OH^-]$ = 2.00×10^{-1} mol dm^{-3}
[Ru(VI)] = 3.66×10^{-6} mol dm^{-3}
μ = 0.25 mol dm^{-3}

[Diethylene glycol] $\times10^2$ mol dm^{-3}	$k_s\times10^6$ mol dm^{-3} min^{-1}	$\left(-\frac{dc}{dt}\right)\times10^6$ mol dm^{-3} min^{-1}	$\frac{k_s}{[\text{Diethylene glycol}]}\times10^4$ min^{-1}
20.00	78.60	78.82	3.93
10.00	44.60	43.96	4.46
6.25	28.38	28.64	4.54
5.00	24.00	24.22	4.80
2.50	13.70	13.14	5.48
2.00	10.24	9.98	5.12

Table 3.144

Temp. = 30°C
$[K_3Fe(CN)_6]$ = 2.00×10^{-3} mol dm^{-3}
$[OH^-]$ = 1.00×10^{-1} mol dm^{-3}
[Ru(VI)] = 3.66×10^{-6} mol dm^{-3}
μ = 0.25 mol dm^{-3}

[Diethylene glycol] $\times10^2$ mol dm^{-3}	$k_s\times10^6$ mol dm^{-3} min^{-1}	$\left(-\frac{dc}{dt}\right)\times10^6$ mol dm^{-3} min^{-1}	$\frac{k_s}{[\text{Diethylene glycol}]}\times10^4$ min^{-1}
20.00	97.31	97.86	4.86
10.00	54.69	54.74	5.46
6.25	38.73	38.12	6.19
5.00	30.71	31.24	6.14
2.50	16.02	16.38	6.40
2.00	11.60	11.40	5.80

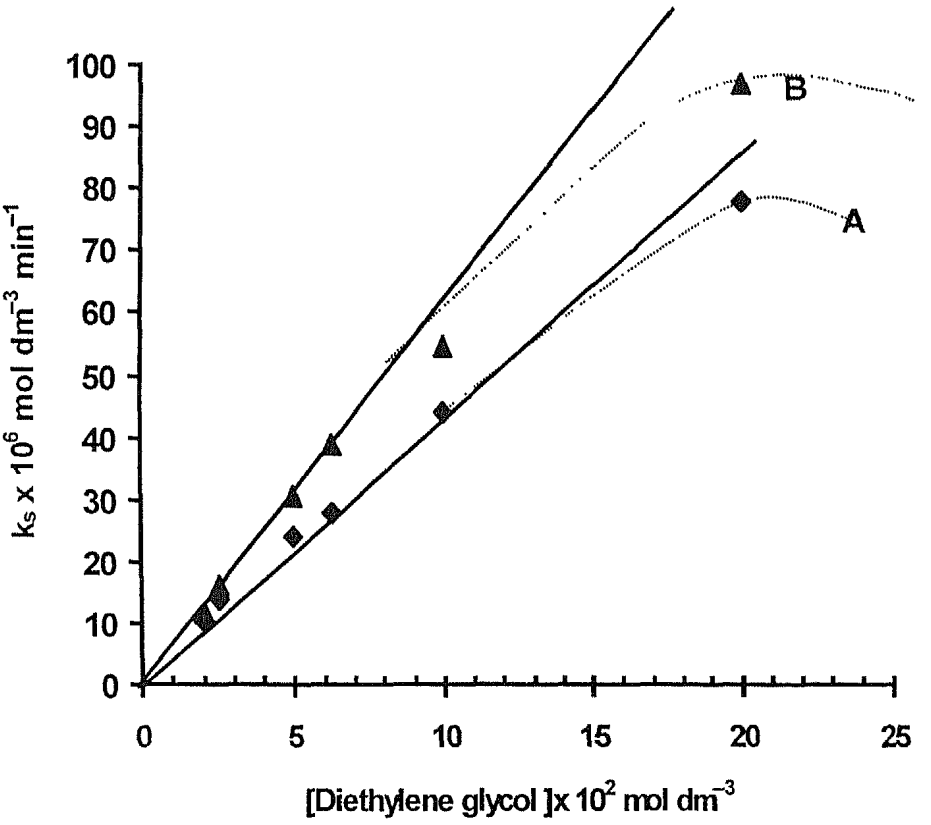


Figure 3.18

Temp.= 30°C; $[K_3Fe(CN)_6] = 2.00 \times 10^{-3}$ mol dm^{-3}; $[OH^-]$= (A) = 2.00×10^{-1} mol dm^{-3}(B) = 1.00×10^{-1} mol dm^{-3}; [Ru(VI)]= 3.66×10^{-6} mol dm^{-3}; $\mu = 0.20$ mol dm^{-3};

The fourth series of the experiment have been performed with triethylene glycol to study the effect of variation of substrate concentration on the reaction velocity. The experiments have been performed by keeping the concentration of other reactants constant and varying the concentration of triethylene glycol. The result thus obtained are given in tables (3.145 to 3.150). The standard zero order rate constant and the value of initial velocity (–dc/dt) have been calculated in the same way as in the preceeding section and the value thus obtained are given below in each tables.

The summarised result are given in the tables (3.151 to 3.152). A close observation of these two tables indicate that reaction velocity increases with increase in triethylene glycol concentration. The results given in tables (3.151 to 3.152) are reproduced in the form of graphs (fig. 3.19(A) to 3.19(B)). These graphs also indicate that the velocity of reaction is directly proportional to the triethylene glycol concentration in the lower range of substrate concentration but at higher concentration deviation occurs and ultimately the reaction velocity tends to attain a constant value.

Table 3.145

Temp. = 35°C

$[K_3Fe(CN)_6]$ = 2.00×10^{-3} mol dm^{-3}

$[OH^-]$ = 1.00×10^{-1} mol dm^{-3}

[Triethylene glycol] = 1.25×10^{-2} mol dm^{-3}

[Ru(VI)] = 4.8×10^{-6} mol dm^{-3}

μ = 0.20 mole dm^{-3}

Time min	$Ce(SO_4)_2$ 1.00×10^{-3}M in ml.	$k_0\times10^2$ ml min^{-1}
1	0.48	
5	0.70	5.5
10	0.96	5.2
20	1.46	5.0
30	1.96	5.0
40	2.48	5.2
50	2.98	5.0
60	3.50	5.2
70	4.00	5.0
80	4.50	5.0
T_∞	10.00	

Average $k_0 = 5.1\times10^{-2}$ ml min^{-1}

A.D. = ± 2.94%

$k_s = 10.20\times10^{-6}$ mole dm^{-3} min^{-1}

$\left(-\frac{dc}{dt}\right) = 10.64\times10^{-6}$ mole $dm^{-3}dm^{-1}$

Table 3.146

Temp. = 35°C

$[K_3Fe(CN)_6]$ = 2.00×10^{-3} mol dm^{-3}

$[OH^-]$ = 1.00×10^{-1} mol dm^{-3}

[Triethylene glycol] = 2.00×10^{-2} mol dm^{-3}

[Ru(VI)] = 4.8×10^{-6} mol dm^{-3}

μ = 0.20 mole dm^{-3}

Time min	$Ce(SO_4)_2$ 1.00×10^{-3}M in ml.	$k_0\times10^2$ ml min^{-1}
1	0.52	
5	0.92	10.0
10	1.40	9.6
15	1.88	9.6
20	2.36	9.6
25	2.86	10.0
30	3.34	9.6
35	3.82	9.6
40	4.30	9.6
45	4.78	9.6
T_∞	10.00	

Average $k_0 = 9.68\times10^{-2}$ ml min^{-1}

A.D. = ± 1.34%

$k_s = 19.36\times10^{-6}$ mole dm^{-3} min^{-1}

$\left(-\frac{dc}{dt}\right) = 19.48\times10^{-6}$ mole $dm^{-3}dm^{-1}$

Table 3.147

Temp. = 35°C

$[K_3Fe(CN)_6]$ = 2.00×10^{-3} mol dm^{-3}

$[OH^-]$ = 1.00×10^{-1} mol dm^{-3}

[Triethylene glycol] = 2.50×10^{-2} mol dm^{-3}

[Ru(VI)] = 4.8×10^{-6} mol dm^{-3}

μ = 0.20 mole dm^{-3}

Time min	$Ce(SO_4)_2$ 1.00×10^{-3}M in ml.	$k_0\times10^2$ ml min^{-1}
1	0.60	
5	1.14	13.5
10	1.82	13.6
15	2.48	13.2
20	3.14	13.2
25	3.80	13.2
30	4.46	13.2
35	5.12	13.2
40	5.78	13.2
45	6.44	13.6
T_∞	10.00	

Average k_0 = 13.27×10^{-2} ml min^{-1}

A.D. = ± 1.05%

k_s = 26.54×10^{-6} mole dm^{-3} min^{-1}

$\left(-\frac{dc}{dt}\right)$ = 26.24×10^{-6} mole $dm^{-3}dm^{-1}$

Table 3.148

Temp. = 35°C

$[K_3Fe(CN)_6]$ = 2.00×10^{-3} mol dm^{-3}

$[OH^-]$ = 1.00×10^{-1} mol dm^{-3}

[Triethylene glycol] = 3.3×10^{-2} mol dm^{-3}

[Ru(VI)] = 4.8×10^{-6} mol dm^{-3}

μ = 0.20 mole dm^{-3}

Time min	$Ce(SO_4)_2$ 1.00×10^{-3}M in ml.	$k_0\times10^2$ ml min^{-1}
1	0.72	
4	1.22	16.6
8	1.88	16.5
12	2.52	16.0
16	3.18	16.5
20	3.82	16.0
24	4.46	16.0
28	5.10	16.0
32	5.70	16.0
36	6.30	16.0
T_∞	10.00	

Average k_0 = 16.17×10^{-2} ml min^{-1}

A.D. = ± 1.42%

k_s = 32.3×10^{-6} mole dm^{-3} min^{-1}

$\left(-\frac{dc}{dt}\right)$ = 32.13×10^{-6} mole $dm^{-3}dm^{-1}$

Table 3.149

Temp. = 35°C
$[K_3Fe(CN)_6]$ = 2.00×10^{-3} mol dm^{-3}
$[OH^-]$ = 1.00×10^{-1} mol dm^{-3}
[Triethylene glycol] = 500×10^{-2} mol dm^{-3}
[Ru(VI)] = 4.8×10^{-6} mol dm^{-3}
μ = 0.20 mole dm^{-3}

Time min	$Ce(SO_4)_2$ 1.00×10^{-3}M in ml.	$k_0\times10^2$ ml min^{-1}
1	0.80	
4	1.50	23.3
7	2.20	23.3
10	2.88	22.6
13	3.58	23.3
16	4.28	24.0
19	5.00	23.3
22	5.70	23.3
25	6.40	22.6
28	7.00	20.0*
T_∞	10.00	

Average $k_0 = 23.2\times10^{-2}$ ml min^{-1}
A.D. = ± 1.20%
$k_s = 47.20\times10^{-6}$ mole dm^{-3} min^{-1}
$\left(-\frac{dc}{dt}\right) = 47.44\times10^{-6}$ mole $dm^{-3}dm^{-1}$

Table 3.150

Temp. = 35°C
$[K_3Fe(CN)_6]$ = 2.00×10^{-3} mol dm^{-3}
$[OH^-]$ = 1.00×10^{-1} mol dm^{-3}
[Triethylene glycol] = 10.0×10^{-2} mol dm^{-3}
[Ru(VI)] = 4.8×10^{-6} mol dm^{-3}
μ = 0.20 mole dm^{-3}

Time min	$Ce(SO_4)_2$ 1.00×10^{-3}M in ml.	$k_0\times10^2$ ml min^{-1}
1	0.90	
3	1.70	40.0
5	2.50	40.0
7	3.28	39.0
9	4.06	39.0
11	4.86	40.0
13	5.66	40.0
15	6.44	39.0
17	7.22	39.0
19	7.82	30.0*
T_∞	10.00	

Average $k_0 = 39.5\times10^{-2}$ ml min^{-1}
A.D. = ± 1.26%
$k_s = 79.0\times10^{-6}$ mole dm^{-3} min^{-1}
$\left(-\frac{dc}{dt}\right) = 79.32\times10^{-6}$ mole $dm^{-3}dm^{-1}$

Table 3.151

Temp. = 30°C
$[K_3Fe(CN)_6]$ = 2.00×10^{-3} mol dm^{-3}
$[OH^-]$ = 10.00×10^{-2} mol dm^{-3}
[Ru(VI)] = 4.81×10^{-6} mol dm^{-3}
μ = 0.20 mol dm^{-3}

[Triethylene glycol] $\times10^2$ mol dm^{-3}	$k_s\times10^6$ mol dm^{-3} min^{-1}	$\left(-\frac{dc}{dt}\right)\times10^6$ mol dm^{-3} min^{-1}	$\frac{k_s}{[\text{Triethylene glycol}]}$ $\times10^4$ min^{-1}
10.00	79.00	79.32	7.90
5.00	47.00	47.44	9.44
3.33	32.30	32.13	9.78
2.50	26.54	26.14	10.60
2.00	19.36	19.48	9.68
1.25	10.20	10.64	8.16

Table 3.152

Temp. = 35°C
$[K_3Fe(CN)_6]$ = 2.00×10^{-3} mol dm^{-3}
$[OH^-]$ = 5.00×10^{-2} mol dm^{-3}
[Ru(VI)] = 4.81×10^{-6} mol dm^{-3}
μ = 0.20 mol dm^{-3}

[Triethylene glycol] $\times10^2$ mol dm^{-3}	$K_s\times10^6$ mol dm^{-3} min^{-1}	$\left(-\frac{dc}{dt}\right)\times10^6$ mol dm^{-3} min^{-1}	$\frac{k_s}{[\text{Triethylene glycol}]}\times10^4$ min^{-1}
10.00	100.00	99.86	10.00
5.00	63.00	63.24	12.60
3.33	49.40	49.36	14.96
2.50	42.40	42.00	16.96
2.00	31.70	31.67	15.85
1.25	18.70	18.50	14.96

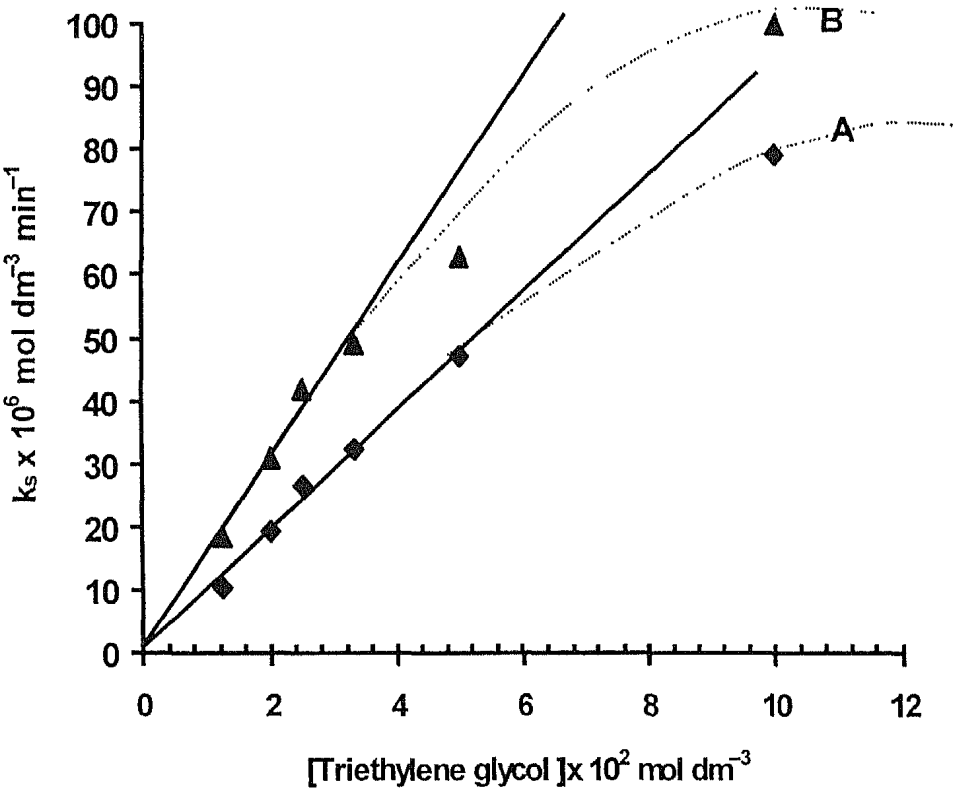


Figure 3.19

Temp.= 35°C; $[K_3Fe(CN)_6] = 2.00 \times 10^{-3}$ mol dm^{-3}; $[OH^-]$= (A) = 10.00×10^{-2} mol dm^{-3}(B) = 5.00×10^{-2} mol dm^{-3}; [Ru(VI)]= 4.81×10^{-6} mol dm^{-3}; $\mu = 0.20$ mol dm^{-3};

The last series of the experiments have been performed with tetraethylene glycol to study the effect of variation of substrate concentration on the reaction velocity. The experiments have been performed by keeping the concentration of other reactants constant and varying the concentration of substrate. The results thus obtained are given in the tables (3.153 to 3.158). The standard zero order rate constant and initial velocity (–dc/dt) have been calculated in the same way as in the preceeding compound and the values thus obtained are given below each table. The summarised results are given in tables (3.159 and 3.160) and have been reproduced in the form of graphs (fig. 3.20(A) and 3.20(B)). These graphs indicate that velocity of reaction is directly proportional to the substrate concentration but at higher but at higher concentration deviation occurs and ultimately the reaction velocity tends to attain a constant value.

Table 3.153

Temp. = 35°C

$[K_3Fe(CN)_6]$ = 2.00×10^{-3} mol dm^{-3}

$[OH^-]$ = 10.0×10^{-2} mol dm^{-3}

[Tetraethylene glycol] = 2.00×10^{-2} mol dm^{-3}

[Ru(VI)] = 6.55×10^{-6} mol dm^{-3}

μ = 0.20 mole dm^{-3}

Time min	$Ce(SO_4)_2$ 1.00×10^{-3}M in ml.	$k_0\times10^2$ ml min^{-1}
1	0.38	
5	0.74	9.0
10	1.20	9.2
15	1.68	9.6
20	2.14	9.2
25	2.60	9.2
30	3.06	9.2
35	3.50	8.8
40	3.96	9.2
45	4.40	8.8
50	4.84	8.8
T_∞	10.00	

Average $k_0 = 9.10\times10^{-2}$ ml min^{-1}

A.D. = ± 2.19%

$k_s = 18.2\times10^{-6}$ mole dm^{-3} min^{-1}

$\left(-\frac{dc}{dt}\right) = 18.26\times10^{-6}$ mole $dm^{-3}dm^{-1}$

Table 3.154

Temp. = 35°C

$[K_3Fe(CN)_6]$ = 2.00×10^{-3} mol dm^{-3}

$[OH^-]$ = 10.0×10^{-2} mol dm^{-3}

[Tetraethylene glycol] = 5.00×10^{-2} mol dm^{-3}

[Ru(VI)] = 6.55×10^{-6} mol dm^{-3}

μ = 0.20 mole dm^{-3}

Time min	$Ce(SO_4)_2$ 1.00×10^{-3}M in ml.	$k_0\times10^2$ ml min^{-1}
1	0.42	
3	0.88	23.0
6	1.56	22.6
9	2.24	22.6
12	2.90	22.0
15	3.58	22.6
18	4.26	22.6
21	4.94	22.6
24	5.60	22.0
27	6.30	23.3
30	6.96	22.0
33	7.46	16.6*
T_∞	10.00	

Average $k_0 = 22.53\times10^{-2}$ ml min^{-1}

A.D. = ± 1.41%

$k_s = 45.06\times10^{-6}$ mole dm^{-3} min^{-1}

$\left(-\frac{dc}{dt}\right) = 45.18\times10^{-6}$ mole $dm^{-3}dm^{-1}$

Table 3.155

Temp. = 35°C

$[K_3Fe(CN)_6]$ = 2.00×10^{-3} mol dm^{-3}

$[OH^-]$ = 10.0×10^{-2} mol dm^{-3}

[Tetraethylene glycol] = 6.25×10^{-2} mol dm^{-3}

[Ru(VI)] = 6.55×10^{-6} mol dm^{-3}

μ = 0.20 mole dm^{-3}

Time min	$Ce(SO_4)_2$ 1.00×10^{-3}M in ml.	$k_0\times10^2$ ml min^{-1}
1	0.48	
3	1.06	29.0
5	1.62	28.0
7	2.20	29.0
9	2.78	29.0
11	3.34	28.0
13	3.90	28.0
15	4.48	28.0
17	5.06	29.0
19	5.62	28.0
21	6.18	28.0
23	6.74	28.0
T_∞	10.00	

Average $k_0 = 28.5\times10^{-2}$ ml min^{-1}

A.D. = ± 1.89%

$k_s = 57.0\times10^{-6}$ mole dm^{-3} min^{-1}

$\left(-\frac{dc}{dt}\right) = 56.86\times10^{-6}$ mole $dm^{-3}dm^{-1}$

Table 3.156

Temp. = 35°C

$[K_3Fe(CN)_6]$ = 2.00×10^{-3} mol dm^{-3}

$[OH^-]$ = 10.0×10^{-2} mol dm^{-3}

[Tetraethylene glycol] = 10.0×10^{-2} mol dm^{-3}

[Ru(VI)] = 6.55×10^{-6} mol dm^{-3}

μ = 0.20 mole dm^{-3}

Time min	$Ce(SO_4)_2$ 1.00×10^{-3}M in ml.	$k_0\times10^2$ ml min^{-1}
1	0.54	
2	1.00	46.0
3	1.46	46.0
4	1.90	44.0
5	2.36	46.0
6	2.80	44.0
7	3.24	44.0
8	3.70	46.0
9	4.16	46.0
10	4.60	44.0
11	5.04	44.0
T_∞	10.00	

Average $k_0 = 45.0\times10^{-2}$ ml min^{-1}

A.D. = ± 2.22%

$k_s = 90.0\times10^{-6}$ mole dm^{-3} min^{-1}

$\left(-\frac{dc}{dt}\right) = 90.12\times10^{-6}$ mole $dm^{-3}dm^{-1}$

Table 3.157

Temp. = 35°C

$[K_3Fe(CN)_6]$ = 2.00×10^{-3} mol dm^{-3}

$[OH^-]$ = 10.0×10^{-2} mol dm^{-3}

[Tetraethylene glycol] = 15.0×10^{-2} mol dm^{-3}

[Ru(VI)] = 6.55×10^{-6} mol dm^{-3}

μ = 0.20 mole dm^{-3}

Time min	$Ce(SO_4)_2$ 1.00×10^{-3}M in ml.	$k_0\times10^2$ ml min^{-1}
1	0.58	
2	1.24	66.0
3	1.90	66.0
4	2.54	64.0
5	3.20	66.0
6	3.84	64.0
7	4.48	64.0
8	5.14	66.0
9	5.80	66.0
10	6.44	64.0
11	7.08	64.0
T_∞	10.00	

Average $k_0 = 65.0\times10^{-2}$ ml min^{-1}

A.D. = ± 1.53%

$k_s = 130.0\times10^{-6}$ mole dm^{-3} min^{-1}

$\left(-\frac{dc}{dt}\right) = 129.74\times10^{-6}$ mole $dm^{-3}dm^{-1}$

Table 3.158

Temp. = 35°C

$[K_3Fe(CN)_6]$ = 2.00×10^{-3} mol dm^{-3}

$[OH^-]$ = 10.0×10^{-2} mol dm^{-3}

[Tetraethylene glycol] = 20.0×10^{-2} mol dm^{-3}

[Ru(VI)] = 6.55×10^{-6} mol dm^{-3}

μ = 0.20 mole dm^{-3}

Time min	$Ce(SO_4)_2$ 1.00×10^{-3}M in ml.	$k_0\times10^2$ ml min^{-1}
1	0.62	
2	1.40	78.0
3	2.20	80.0
4	3.00	80.0
5	3.78	78.0
6	4.56	78.0
7	5.32	76.0
8	6.08	76.0
9	6.86	78.0
10	7.26	40.0*
T_∞	10.00	

Average $k_0 = 78.0\times10^{-2}$ ml min^{-1}

A.D. = ± 1.28%

$k_s = 156.0\times10^{-6}$ mole dm^{-3} min^{-1}

$\left(-\frac{dc}{dt}\right) = 155.94\times10^{-6}$ mole $dm^{-3}dm^{-1}$

Table 3.159

Temp. = 35°C
$[K_3Fe(CN)_6]$ = 2.00×10^{-3} mol dm^{-3}
$[OH^-]$ = 10.00×10^{-2} mol dm^{-3}
[Ru(VI)] = 6.55×10^{-6} mol dm^{-3}
μ = 0.20 mol dm^{-3}

[Tetraethylene glycol] $\times10^2$ mol dm^{-3}	$k_s\times10^6$ mol dm^{-3} min^{-1}	$\left(-\frac{dc}{dt}\right)\times10^6$ mol dm^{-3} min^{-1}	$\frac{k_s}{[\text{Tetraethylene glycol}]}$ $\times10^4$ min^{-1}
20.00	156.00	155.94	7.80
15.00	130.00	129.74	8.66
10.00	90.00	90.12	9.00
6.25	57.00	56.86	93.12
5.00	45.06	45.18	9.00
2.00	18.20	18.26	9.10

Table 3.160

Temp. = 35°C
$[K_3Fe(CN)_6]$ = 2.00×10^{-3} mol dm^{-3}
$[OH^-]$ = 20.00×10^{-2} mol dm^{-3}
[Ru(VI)] = 6.55×10^{-6} mol dm^{-3}
μ = 0.20 mol dm^{-3}

[Tetraethylene glycol] $\times10^2$ mol dm^{-3}	$K_s\times10^6$ mol dm^{-3} min^{-1}	$\left(-\frac{dc}{dt}\right)\times10^6$ mol dm^{-3} min^{-1}	$\frac{k_s}{[\text{Tetraehtylene glycol}]}$ $\times10^4$ min^{-1}
20.00	90.0	89.90	4.50
15.00	67.0	67.16	4.46
10.00	46.0	45.98	4.60
6.25	28.0	28.12	4.48
5.00	23.0	22.92	4.60
2.00	8.5	8.74	4.25

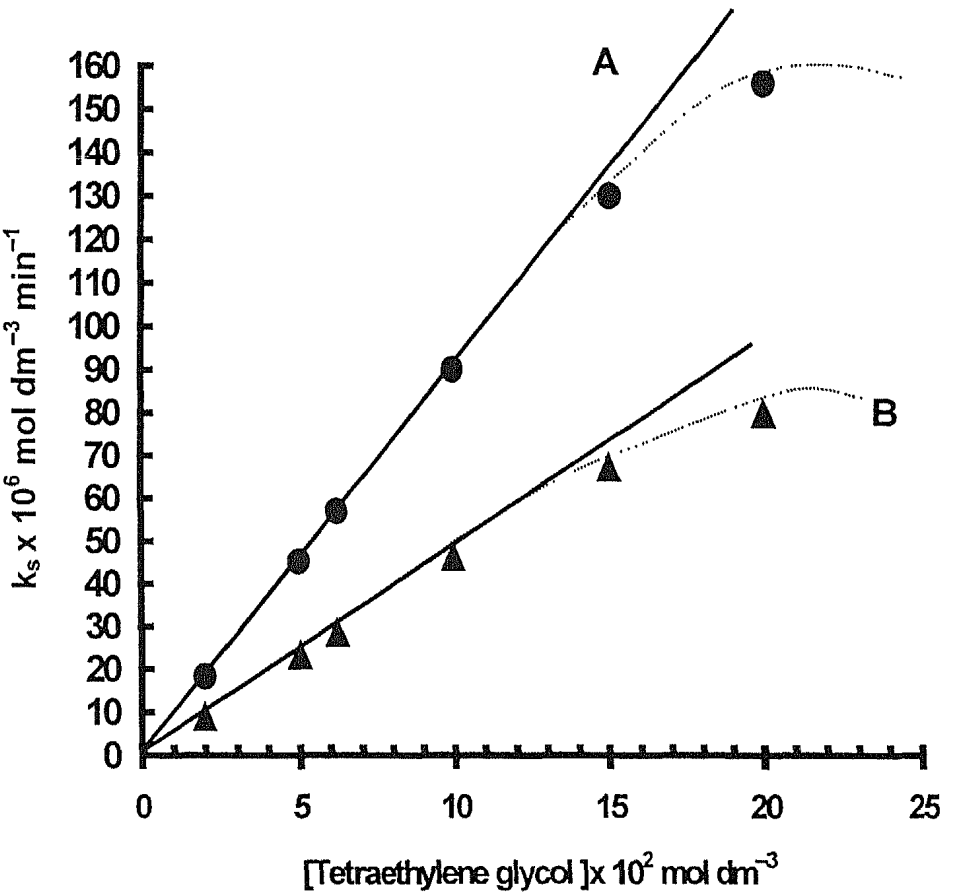


Figure 3.20

Temp.= 35°C; $[K_3Fe(CN)_6] = 2.00 \times 10^{-3}$ mol dm^{-3}; $[OH^-]$= (A) = 10.00×10^{-2} mol dm^{-3}(B) = 5.00×10^{-2} mol dm^{-3}; [Ru(VI)]= 6.55×10^{-6} mol dm^{-3}; $\mu = 0.20$ mol dm^{-3};

CHAPTER - IV

EFFECT OF TEMPERATURE

4.1 THE EFFECT OF TEMPERATURE ON THE RATE OF THE REACTION:

In this chapter the effect of variation of temperature on Ru(VI) catalysed oxidation of 4-methyl pentanol-2, 2-methoxy ethanol, diethylene glycol, triethylene glycol and tetraethylene glycol has been studied.

The experiments were carried at different concentrations of organic substrates by keeping the concentration of other reactants constant viz. hexacyanoferrate(III), hydroxyl ion, ruthenate ion at constant ionic strength. The results thus obtained at four different temperature are summarised in tables (4.1) to (4.5).

Table 4.1

$[K_3Fe(CN)_6]$ = 2.00×10^{-3} mole dm^{-3}

$[OH^-]$ = 10.0×10^{-2} mole dm^{-3}

[Ru(VI)] = 2.18×10^{-6} mole dm^{-3}

μ = 0.25 mole dm^{-3}

[4-methyl pentanol-2]$\times10^2$ mole dm^{-3}	$k_s \times 10^6$ mole dm^{-3} min^{-1}			
	θ/25°C	θ/30°C	θ/35°C	θ/40°C
8.30	20.00	32.00	50.00	80.00
5.00	12.97	20.40	33.00	50.00
2.50	8.57	14.00	21.00	37.00
1.25	5.32	7.50	14.02	22.95
0.83	3.50	5.25	8.25	13.00

Table 4.2

$[K_3Fe(CN)_6]$ = 2.00×10^{-3} mole dm^{-3}

$[OH^-]$ = 10.0×10^{-2} mole dm^{-3}

[Ru(VI)] = 15.5×10^{-7} mole dm^{-3}

μ = 0.20 mole dm^{-3}

[2-methoxy ethanol]$\times10^2$ mole dm^{-3}	$k_s \times 10^6$ mole dm^{-3} min^{-1}			
	θ/25°C	θ/30°C	θ/35°C	θ/40°C
10.00	36.60	51.20	70.00	97.80
5.00	20.50	29.08	39.60	53.80
2.50	11.20	15.84	21.40	30.20
1.25	5.20	7.20	10.40	14.20
0.83	3.08	4.12	5.80	7.95

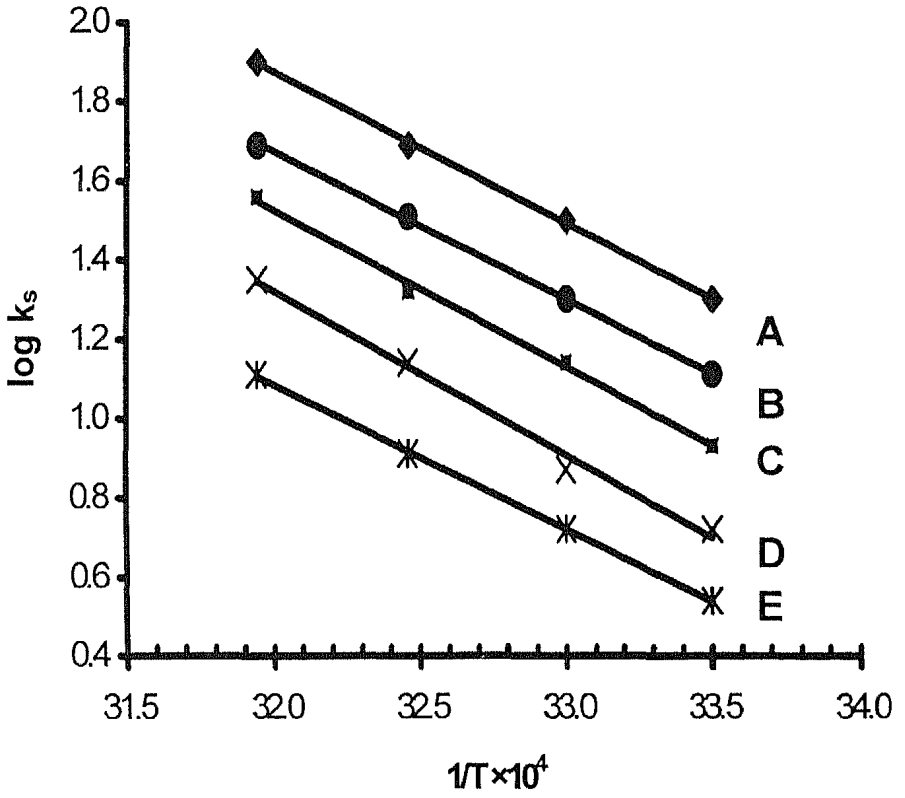


Figure 4.1 $[K_3Fe(CN)_6] = 2.00 \times 10^{-3}$ mol dm^{-3}; [Ru(VI)] = 2.18×10^{-6} mol dm^{-3} ; [OH^-]=1.00×10^{-1} mol dm^{-3}; μ = 0.25 mol dm^{-3}
[4-Methyl Pentanol-2] $\times 10^2$ mol dm^{-3}
(A) 8.3
(B) 5.0
(C) 2.5
(D) 1.25
(E) 0.83

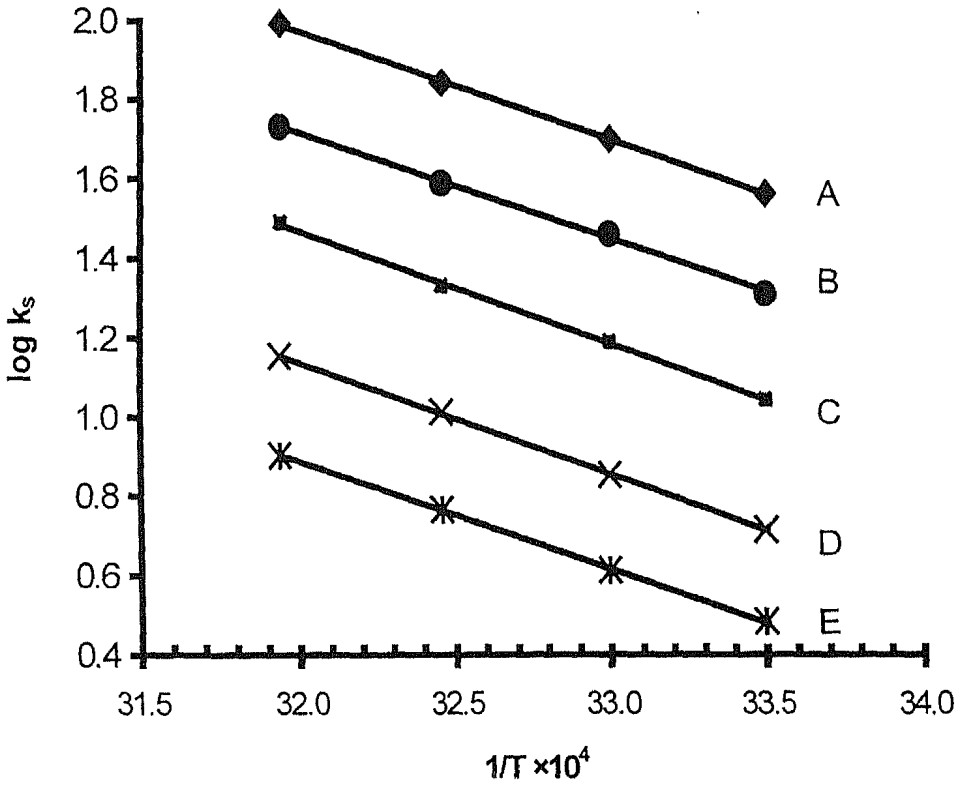


Figure 4.2 $[K_3Fe(CN)_6] = 2.00 \times 10^{-3}$ mol dm^{-3}; $[Ru(VI)] = 15.5 \times 10^{-7}$ mol dm^{-3} ; $[OH^-] = 1.00 \times 10^{-1}$ mol dm^{-3}; $\mu = 0.25$ mol dm^{-3}
[2-Methoxy ethanol] $\times 10^2$ mol dm^{-3}
(A) 10.00
(B) 5.00
(C) 2.50
(D) 1.25
(E) 0.83

Table 4.3

$[K_3Fe(CN)_6]$ = 2.00×10^{-3} mole dm^{-3}

$[OH^-]$ = 20.0×10^{-2} mole dm^{-3}

[Ru(VI)] = 3.66×10^{-6} mole dm^{-3}

μ = 0.25 mole dm^{-3}

[Diethylene glycol]$\times10^2$ mole dm^{-3}	$k_s \times 10^6$ mole dm^{-3} min^{-1}			
	θ/30°C	θ/35°C	θ/40°C	θ/45°C
1.25	8.80	11.30	15.70	21.00
2.50	13.20	17.40	23.70	30.20
5.00	20.30	26.70	40.30	52.50
6.25	25.10	36.40	53.00	74.50
10.00	34.70	47.70	66.10	97.80
20.00	62.90	81.30	118.80	172.10

Table 4.4

$[K_3Fe(CN)_6]$ = 2.00×10^{-3} mole dm^{-3}

$[OH^-]$ = 10.0×10^{-2} mole dm^{-3}

[Ru(VI)] = 4.81×10^{-6} mole dm^{-3}

μ = 0.20 mole dm^{-3}

[Triethylene glycol]$\times10^2$ mole dm^{-3}	$k_s \times 10^6$ mole dm^{-3} min^{-1}			
	θ/25°C	θ/30°C	θ/35°C	θ/40°C
10.00	38.40	56.00	79.00	111.20
5.00	23.04	32.56	47.10	66.00
2.50	13.02	18.72	26.54	36.36
1.25	4.18	7.02	10.30	14.78
0.83	2.90	3.80	5.60	8.12

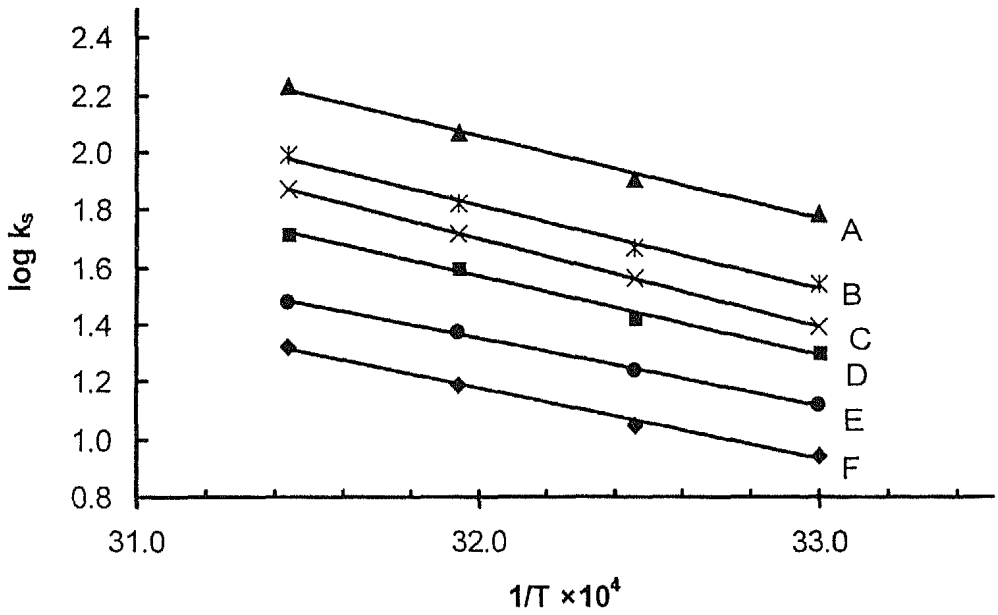


Figure 4.3 **[$K_3Fe(CN)_6$] = 2.00 ×10^{-3} mol dm^{-3}; [Ru(VI)] = 3.66 × 10^{-6} mol dm^{-3} ; [OH^-]=2.00×10^{-1} mol dm^{-3} ; μ = 0.25 mol dm^{-3}**
[Diethylene Glycol] ×10^2 mol dm^{-3}
(A) 20.0
(B) 10.0
(C) 6.25
(D) 5.0
(E) 2.50
(F) 1.25

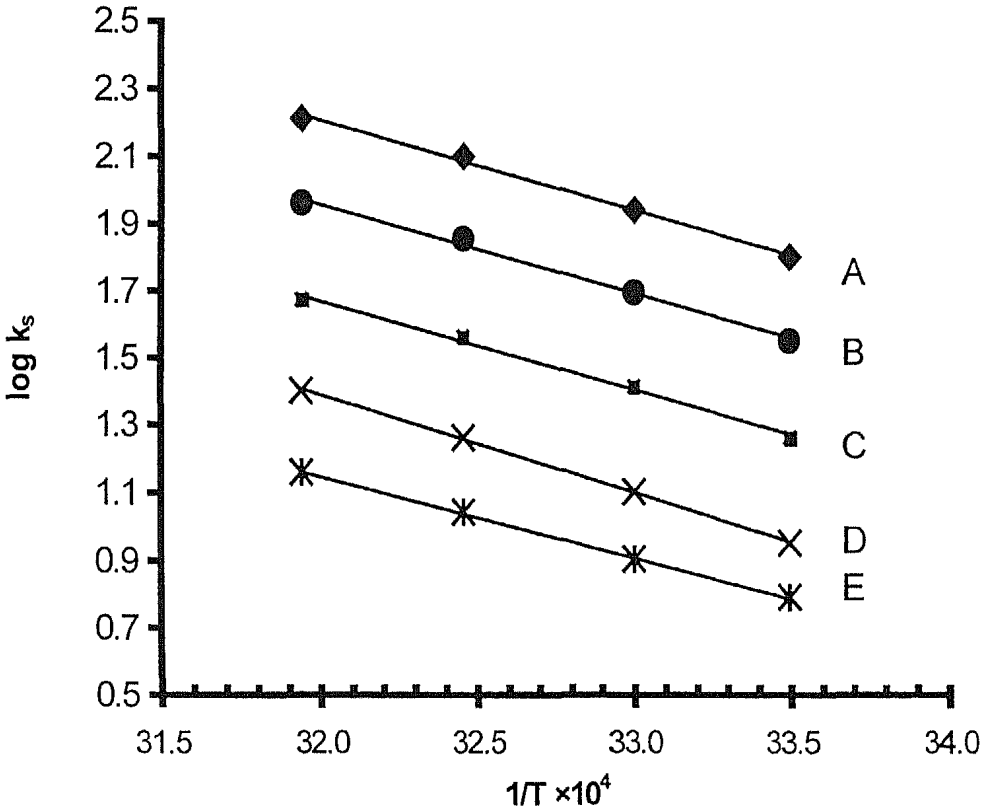


Figure 4.4 **$[K_3Fe(CN)_6] = 2.00 \times 10^{-3}$ mol dm^{-3}; [Ru(VI)] = 4.81×10^{-6} mol dm^{-3}; [OH$^-$]=1.00×10^{-1} mol dm^{-3}; ; μ = 0.25 mol dm^{-3}**
[Triethylene Glycol] $\times 10^2$ mol dm^{-3}
(A) 10.00
(B) 5.00
(C) 2.50
(D) 1.25
(E) 0.83

Table 4.5

$[K_3Fe(CN)_6]$ = 2.00×10^{-3} mole dm^{-3}

$[OH^-]$ = 10.0×10^{-2} mole dm^{-3}

[Ru(VI)] = 6.55×10^{-6} mole dm^{-3}

μ = 0.20 mole dm^{-3}

[Tetraethylene glycol]$\times10^2$ mole dm^{-3}	$k_s \times 10^6$ mole dm^{-3} min^{-1}			
	θ/25°C	θ/30°C	θ/35°C	θ/40°C
20.00	63.10	87.10	127.00	163.00
10.00	35.50	49.00	70.80	91.20
5.00	18.80	25.80	36.40	46.80
2.00	8.92	12.60	18.20	25.20
1.00	6.17	7.95	11.00	14.50

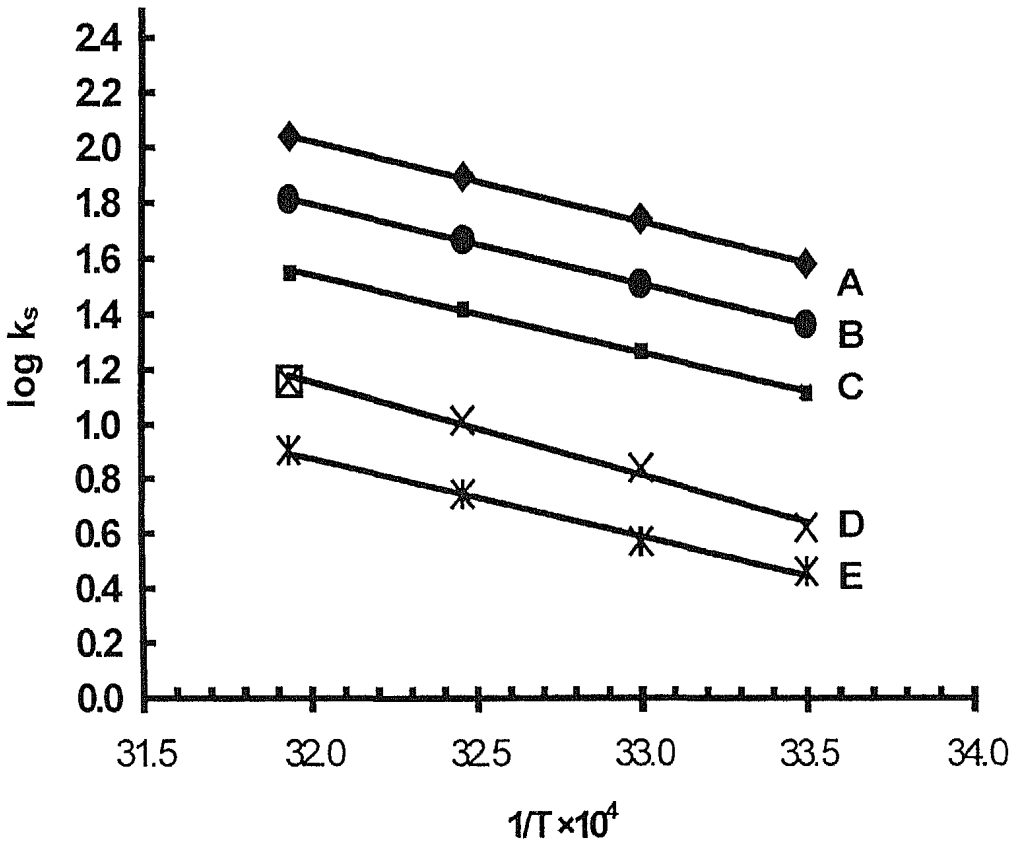


Figure 4.5 $[K_3Fe(CN)_6] = 2.00 \times 10^{-3}$ mol dm^{-3}; [Ru(VI)] = 6.55×10^{-6} mol dm^{-3} ; $[OH^-] = 1.00 \times 10^{-1}$ mol dm^{-3}; $\mu = 0.20$ mol dm^{-3}
[Tetraethylene Glycol] $\times 10^2$ mol dm^{-3}
(A) 20.00
(B) 10.00
(C) 5.00
(D) 2.00
(E) 1.00

In order to calculate the energy of activation ΔE, the experiments have been performed under identical conditions at different temperatures. The effect of temperature on the reaction rate is expressed by Arrhenious equation.

$$k_{sp} = A.\, E^{-\Delta E/RT} \tag{4.1}$$

Where k_{sp} represents specific rate constant, A is frequency factor, ΔE is energy of activation, R is gas constant and T is the absolute temperature. Equation (4.1) can be re-written as –

$$\log k_{sp} = \log A - \frac{\Delta E}{2.303\ RT} \tag{4.2}$$

When a graph is plotted between log k_s and (I/T), a straight line with a slope equal to -ΔE/2.303 RT is obtained (fig. (4.1) to (4.5)). The value of energy of activation has been calculated from this slope and the values are given in table (4.6).

The value of log A has been calculated from the equation (4.2) i.e.,

$$\log A = \log k_{sp} + \frac{\Delta E}{2.303\ RT} \tag{4.3}$$

Where k_{sp} is obtained by the following relation

$$k_{sp} = \frac{k_s}{[\text{substrate}]\ [\text{catalyst}]}$$

The entropy of activation ΔS has been calculated by employing the equation.

$$k_{sp} = e.^{kT/h},\quad e^{\Delta S^{\#}/R},\quad e^{-\Delta E/RT} \tag{4.4}$$

Where k and h are Boltz mann's and Planck's constant. ($k=1.3805\times10^{-16}$ ergs deg^{-1} $mole^{-1}$ and $h = 6.625\times10^{-27}$ ergs sec.) respectively and T is absolute temperature.

Comparing equation (4.1) and (4.4) the following expression is obtained.

$$A = e^{kT/h} \quad e^{\Delta s^{\neq}/R}$$

$$\text{or} \quad \log_{10} A = \log_{10}(ek/h) + \log T + \frac{\Delta s^{\neq}}{2.303R}$$

$$\text{or} \quad \Delta s^{\neq} = [2.303R \log_{10} A - \log_{10} T - \log_{10}(ek/h)]$$

$$\text{or} \quad \Delta s^{\neq} = [4.576 \log_{10} A - \log_{10} T - 10.753] \qquad (4.5)$$

The value of the entropy of activation ($\Delta S^{\neq}$) have thus been calculated from equation (4.5).

The free energy of activation $\Delta F^{\neq}$ has been calculated by using the equation.

$$\Delta F^{\neq} = \Delta H - T\Delta S^{\neq} \qquad (4.6)$$

In the case of solution, the change in volume is negligible hence $\Delta H = \Delta E$.

Therefore equation (4.6) can be re-written as

$$\Delta F^{\neq} = \Delta E - T\Delta S^{\neq} \qquad (4.7)$$

The value of $\Delta F^{\neq}$, for different compound, have been calculated from the above equation (4.7). The value of ΔE, ΔH, $\Delta S^{\neq}$ and $\Delta F^{\neq}$ thus obtained have been given in the following tables (4.6) and (4.7).

Table 4.6

Name of the compound	ΔE K, Cal $mole^{-1}$
4-methyl pentanol-2	26.08
2-methoxy ethanol	29.62
Diethylene glycol	25.86
Triethylene glycol	22.72
Tetraethylene glycol	22.05

Thermodynamic Parameters of Various Compounds.

Table 4.7

Name of the compound	$\Delta H^{\neq}$ KJ $mole^{-1}$	$\Delta S^{\neq}$ e.u.	$\Delta F^{\neq}$ KJ $mole^{-1}$
4-methyl pentanol-2	109.10	2.27	111.94
2-methoxy ethanol	123.10	1.36	125.60
Diethylene glycol	108.10	2.37	111.06
Triethylene glycol	95.06	3.15	99.00
Tetraethylene glycol	92.25	3.40	96.50

The perusal of the table (4.7) shows that the value of ΔF are very close for all the compounds. Therefore, on qualitative basis, one can say that all reactions are taking place through similar route.

CHAPTER - V

DISCUSSION AND INTERPRETATION OF RESULT

DISCUSSION AND INTERPRETATION

5.1 PRELIMINARY REMARKS

A detailed survey of the experimental results, given in second, third and fourth chapter, reveals that the ruthenate ion catalysed oxidation of alcohols are quite similar in nature as regards to the oxidative feature. The products analysis given in second chapter clearly indicates that the corresponding acids are produced in case of 2-methoxy ethanol, diethylene glycol, triethylene glycol and tetraethylene glycol, while corresponding ketone in case of 4-methyl pentanol-2, during the reaction. The magnitude of the activation energy in each case suggests that all the reactions proceed by a common route. With these ideas, the probable path of reaction has been proposed in subsequent pages in order to explain the experimental results and the rate expression has been derived.

5.2 GENERAL FEATURE OF RU(VI) CATALYSED REACTION:

In order to elucidate the actual mechanistic path for ruthenium (VI) catalysed oxidation of 4-methyl pentanol-2, 2-methoxy ethanol, diethylene glycol, triethylene glycol and tetraethylene glycol with alkaline hexacyanoferrate(III), the reaction order with respect to each reacting species has been determined kinetically and given in third chapter and thus results obtained will lead to following conclusions:

1. The reaction follows zero order kinetics with respect to hexacyanoferrate(III) (Fig. 3.1 to 3.5 and tables 3.1 to 3.40) upto eight folds variation of its concentration.

2. The order of reaction with respect to catalyst (ruthenate ion) is unity

See reference on Pg. No. 165

(Fig. 3.6 to 3.10) to Tables 3.41 to 3.80.

3. The velocity of the reaction has linear proportionality with substrate concentration in lower range of concentration but at higher concentration of substrate, a deviation occurs and it seems that velocity attains a constant value (Fig. 3.16 to 3.20).

4. The velocity of the reaction is retarded on increasing the concentration of hydroxide ions, (Fig. 3.11, 3.15).

5.3 ACTUAL SPECIES OF RUTHENIUM DURING THE REACTION

Before proceeding for mechanistic details, it is worthwhile at this stage to discuss the actual species of the catalyst. The preparation of sodium ruthenate is given in second chapter. There it has clearly been mentioned that ruthenium tetraoxide was converted into sodium ruthenate by the action of carbonate free alkali (NaOH). The concentration of ruthenate ion was determined by measuring, the absorbance at 460nm, 1820 cm^{-1} m^{-1} being its molar absorbity coefficient.

Connick et al.[1] observed that orange solution of sodium ruthenate, in approximately 1M sodium hydroxide, gives no sign of precipitation in more than one year. We have also observed that our solution of sodium ruthenate has shown no sign of precipitation for at least six months. Inspite of the stability of sodium ruthenate, it was prepared before studying each compound. It has also been reported by Latimer[2] that ruthenate ion remains stable in 1M sodium hydroxide but if the pH is lowered to about 12, the following reaction may take place:

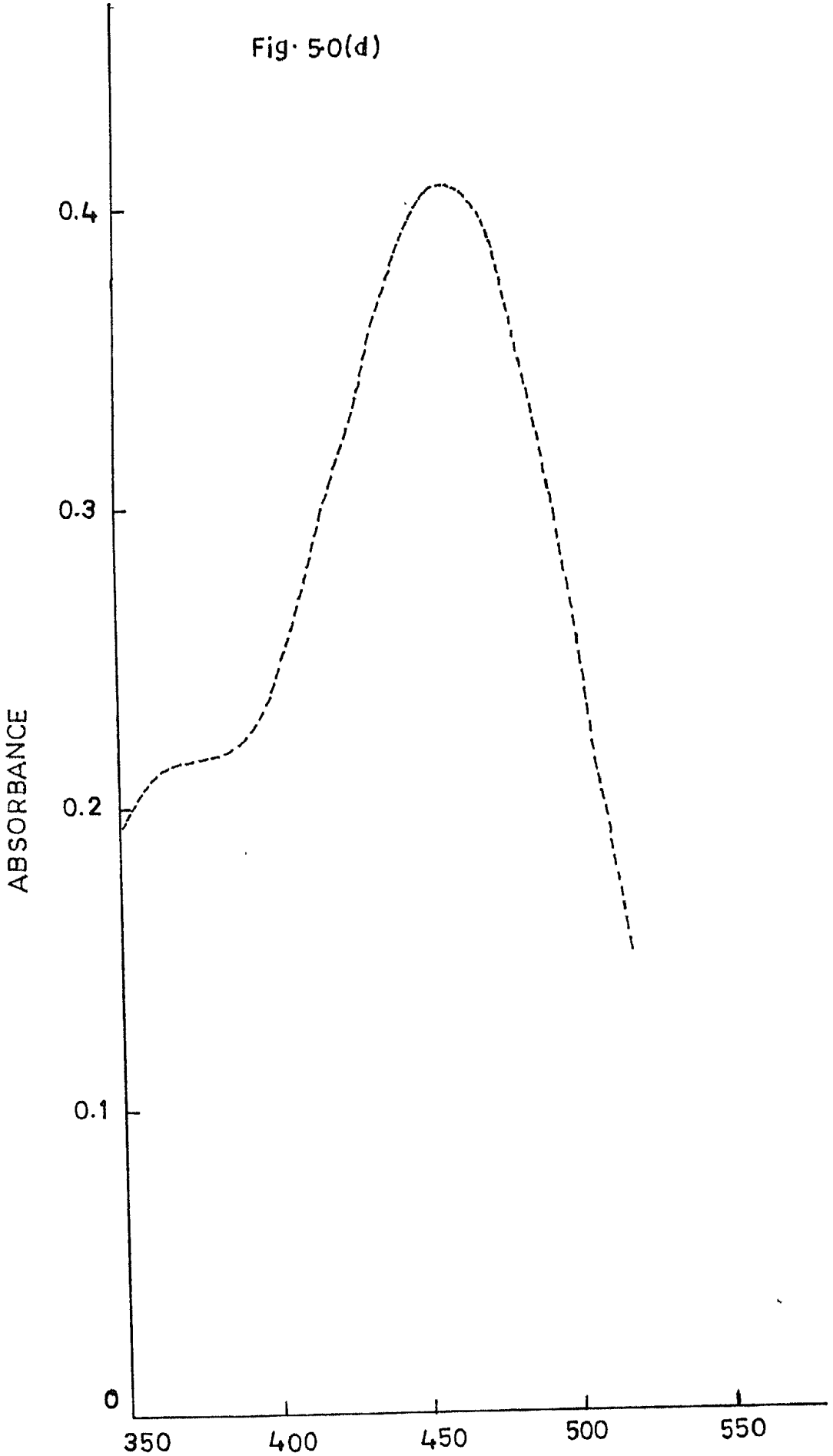
$$3\ RuO_4^{2-} + 2H_2O \rightleftharpoons 2\,RuO_4^{-1} + RuO_2 + 4OH^-$$

Moreover, Syman et al[3] have reported that if the ruthenate solution was boiled after dilution with water, there is no formation of per-ruthenate as reported by Latimer[2] we have also observed that if the ruthenate solution is diluted by water and other precautions are taken, there is no sign of precipitation of ruthenium dioxide but if this solution is kept for more than six months the slight turbidity appears. But to be more sure that ruthenate may not disproportionate into per-ruthenate and ruthenate dioxide, the concentration of sodium hydroxide was kept such that the pH of the reaction mixture was never lowered than 12.

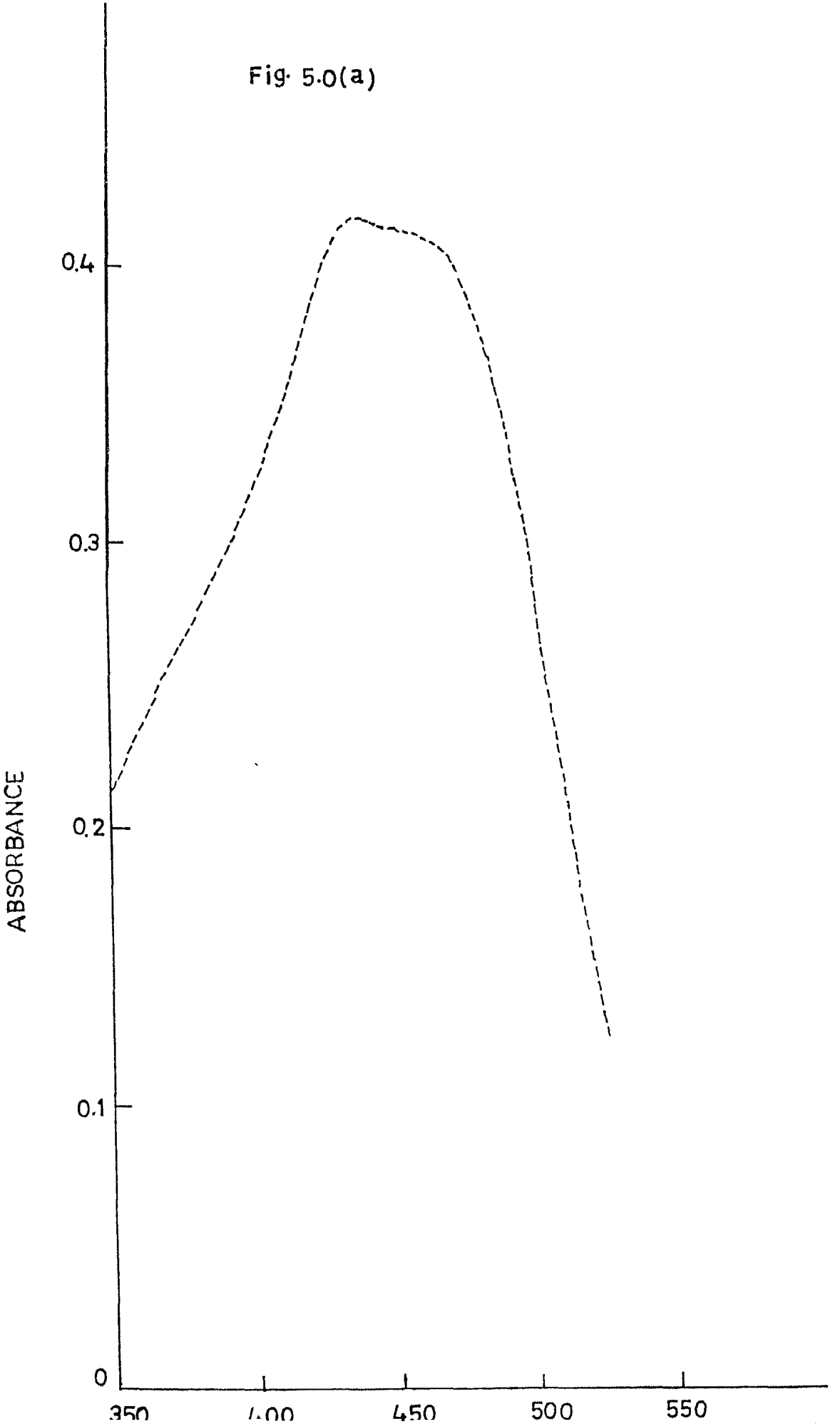
In order to see whether ruthenate ion i.e. ruthenium (VI) is changed into perruthenate ion i.e. ruthenium (VII) or ruthenium tetraoxide, i.e. ruthenium (VIII) by action of alkaline hexacyanoferrate(III) during the reaction, few experiments have been performed by taking ruthenate ion and different amounts of hexacyanoferrate(III). After keeping this mixture for two hours, the spectra has been recorded. Firstly, the spectra of pure solution of sodium ruthenate has been recorded which comes out to be identical with the spectra given in chapter second (fig. 2.1) and the subsequent experiments with different amount of hexacyanoferrate(III) have been added to fixed amount of sodium ruthanate and spectra has been recorded. Spectra (fig. 5.0(d)) has been obtained when the concentration of ruthenate ion is greater than concentration of hexacyanoferrate(III) and in (fig. 5.0(a)) the concentration of hexacyanoferrate(III) is such that the product of absorbity coefficient and concentration is equal to the product of absorbity coefficient and concentration of ruthenate ion, therefore, more or less equal absorbance is obtained in spectra, (fig. 5.0(b)). The concentration of hexacyanoferrate(III) is slightly greater than the concentration of ruthenate ion that is why the peak at 425 nm is more predominant and in another set

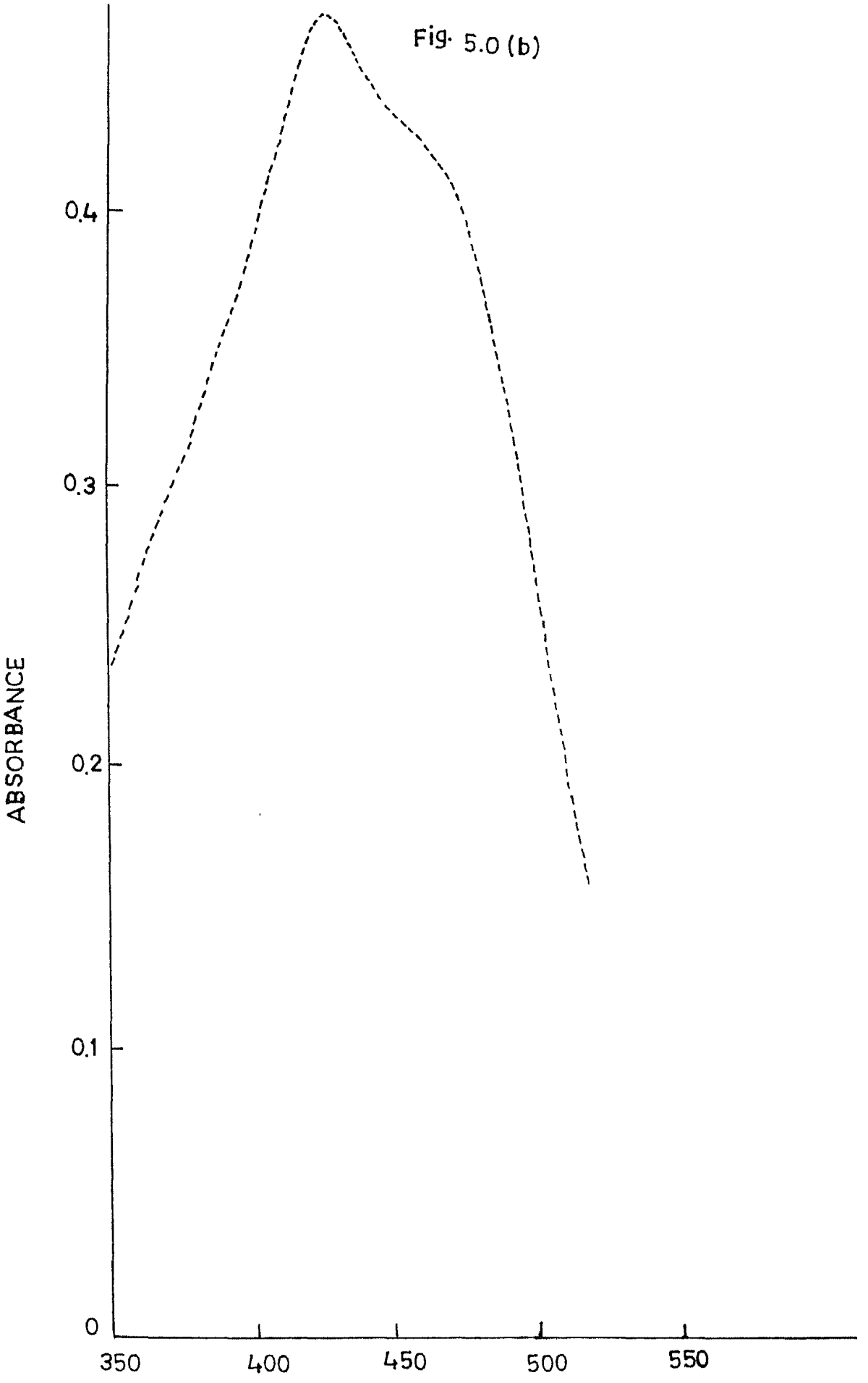
See reference on Pg. No. 165

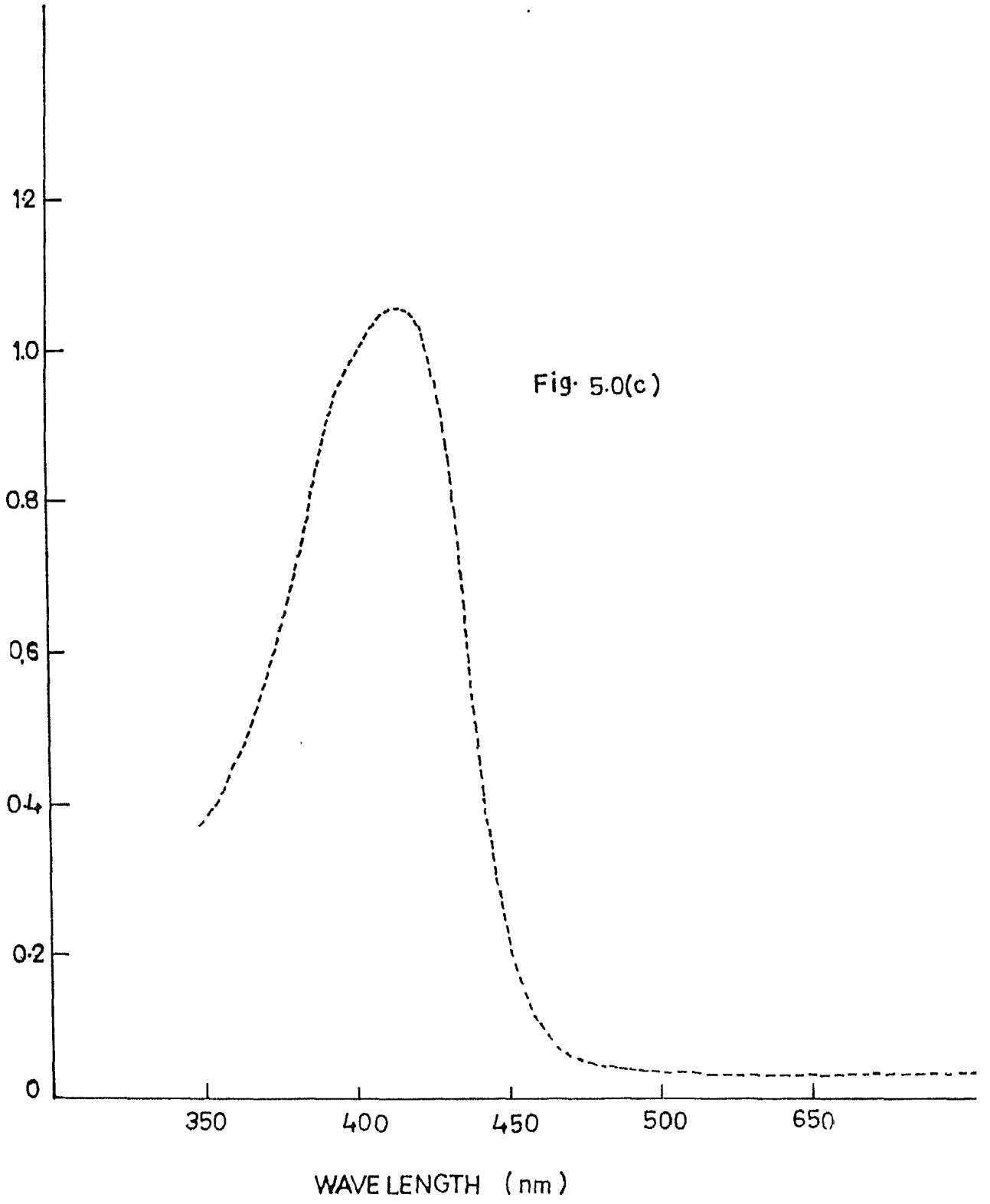
Fig· 50(d)



Fig· 5.0(a)




Fig. 5.0 (b)
ABSORBANCE
0.4
0.3
0.2
0.1
0
350
400
450
500
550



Fig· 5.0(c)

the concentration of hexacyanoferrate(III) is much greater than concentration of ruthenate ion and the spectra obtained is same as obtained in case of pure hexacyanoferrate (III) (fig. 5.0(c)). On comparing all the three spectra (fig. 5.0(d, a, b)) it is quite clear that the absorbance corresponding to the of ruthenate ion is same in all spectra (λ_{max} 460nm) which clearly proves that ruthenate ion i.e., ruthenium(VI) is not being oxidixed to ruthenium (VII) or (VIII). Apart from this spectrum has also been recorded in ultra violet region so as to ascertain the presence of ruthenium (VII) or (VIII) which may be produced due to the oxidation of ruthenate ion, ruthenium (VI) by alkaline hexacyanoferrate(III), then a peak should be obtained at 310nm because ruthenium (VII) or (VIII) have absorbity coefficient as 2445 cm^{-1} and 2060 cm^{-1} respectively but no peak at 310 nm is obtained. Therefore, it has been concluded that ruthenium is present as ruthenate ion, i.e., ruthenium (VI) during the reactions.

The electronic spectra[4] studies have confirmed that lower oxidation state of ruthenium exists in the hydrated form, as $Ru(H_2O)_6^{3+}$, but the higher oxidation states are not strongly solvated. There is a close similarity between ruthenium and manganese in the oxo ions both MO_4^- and MO_4^{-2} being known where M stands for Ru or Mn, oxo ions are having tetrahedral geometry and co-ordination number four. If osmium and ruthenium tetraoxide are dissolved in alkali, they behave in a quite different manner. Ruthenium tetraoxide is reduced by hydroxide ion to ruthenium(VI)[5] while osmium tetraoxide gives $[OSO_4(OH)_2]^{2-}$. This difference between Ru and Os appears to be due to the ability of 5d metal oxo anion to increase the co-ordination shell. In case of osmium, $K_2[OSO_4(OH)_2]$ can be isolated but in the case of ruthenium similar compound cannot be isolated. On the other

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hand in the solution of sodium hydroxide the formation of corresponding ruthenate is well known.

There is no evidence for addition of OH^- ion to 3d metal oxo anions[7] but in the case of reaction between per-ruthenate and manganate ion in alkaline medium, it was suggested that one or more of the anions could possibly have hydroxide ion associated with them and coordination of OH^- ion with per-ruthenate upto lower extent has also been suggested by Syman and Coworkers[3] during the kinetic study of decomposition of per-ruthenate ion in alkaline medium therefore during the kinetic study it can be assumed that ruthenium(VI) remains as ruthenate ion i.e., RuO_4^{-2}.

To be more sure about the species of ruthenium the absorbance at 460nm and 385nm was measured. The ratio of the absorbance at 460nm and 385nm has been found as 2.07 corresponding to pure ruthenate[6] at different concentrations of sodium hydroxide as low as upto 0.01M. It is evident from the figures (3.11) to (3.15) and the data recorded in the section (3.3) that the rate of the reaction increases as the concentration of hydroxyl ion decreases. This type of observation have been made in the case of ruthenium(III) catalysed oxidation of organic compounds by hexacyanoferrate(III) in alkaline medium which is explained on the basis of the assumption that ruthenium(III) in aqueous alkaline solution exist[7] as $Ru(H_2O)OH^{2+}$.

During the study of oxidation of some unsaturated compounds by sodium ruthenate[8], it has been observed that finally ruthenium(VI) is reduced to ruthenium(IV). To be more precise, that during our reactions whether ruthenium(VI) is reduced to ruthenium(IV) or not, a few experiments were performed without addition of hexacyanoferrate(III) and

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thus produced black precipitate has been washed by water many times in gooch crucible and mixed with little alkali and hexacyanoferrate(III). Resulted solution is capable of acting as catalyst.

The experimental results given in the second chapter and sections 3.1 to 3.4 in third chapter show that the velocity is nearly linear proportional with substrate concentration in its lower range of concentration but at higher concentration of substrate, a deviation occurs it seems that velocity attains a constants value and moreover Michaelis and Menten[9] plots were obtained which indicate that the complex formation might take place with the substrate molecule. The gradual decrease of reaction velocity with increase of hydroxide ion can be explained by two assumptions. Firstly during the kinetic study of oxidation of some unsaturated compounds by ruthenate ion in alkaline medium, Lee et al.[10] has suggested the retardation in velocity on increasing the concentration of hydroxyl ion on the basis of protonation of ruthenate ion because of comparison with oxy anions, it is reasonable to expect that protonation would increase the vigour of oxidation[11]. We feel that protonation of oxidant like $MO_4^{(x+1)-1}$, where M stands for Mn or Ru and X may be zero or one, in acidic medium is correct, but as soon as the medium becomes alkaline the proton will be taken by a nucleophilic like OH^- ion. Secondly, hydroxyl ion may be present in the right hand side of reversible step. This can only be possible when all ruthenate ions are present as $(RuO_4.OH)^{-3}$.

As we have discussed earlier that coordination of hydroxyl ion with ruthenate ion or per ruthenate ion is not common but Syman[3] and Coworkers have suggested the coordination of hydroxyl ion with per-ruthenate ion during the kinetic study. During the study of reaction between aqueous

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media, it was suggested that one or more of the anions could possibly have hydroxyl ion associated with them. Hydroxide ion association may be represented by the equilibrium –

$$MO_4^{x-} + OH^- \rightleftharpoons MO_4.OH^{(x+1)}$$

Where M is Ru or Mn and x is one or two depending upon the oxidation state. The negative value of the entropy suggests that the equilibrium constant for above reaction should be larger for ruthenate and permanganate than for per-ruthenate and manganate[12]. If the formation constant for $MO_4.OH^{(x+1)-1}$ is large, no effect of varying $[OH^-]$ would be pronounced. During these studies the estimate of the rearrangement energy is undoubtedly low especially in view of the possible hydroxide ion association with one or more of anions. On the basis of above discussion it will be fair to assume that some of the ruthenate ion may be present as $(RuO_4.OH)^{-3}$. In all studied reactions, it has been observed that alkali has appreciable effect on the rate of reaction, therefore, ruthenate ion can exist according to following reactions.

$$RuO_4^{-2} + OH^- \rightleftharpoons (RuO_4.OH)^{-3}$$

Thus in the light of above observations the following probable steps for ruthenate ion catalysed oxidation of studied organic substrates have been proposed as follows:

$$RuO_4^{-2} + OH^- \overset{K}{\rightleftharpoons} (RuO_4.OH)^{-3} \qquad \text{(i)}$$

$$RuO_4^{-2} + S \overset{K_1}{\rightleftharpoons} (S.RuO_4)^{-2} \qquad \text{(ii)}$$

complex

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$$(S.RuO_4)^{-2} \xrightarrow[xH_2O]{k} RuO_2.xH_2O + \text{Intermediate product} + 2OH^- \quad \text{(iii)}$$

$$RuO_2.xH_2O + 2Fe(CN)_6^{-3} + 4OH^- \xrightarrow{\text{fast}} RuO_4^{-2} + 2Fe(CN)_6^{-4} + (x+2)H_2O \quad \text{(iv)}$$

$$\text{Intermediate product} \xrightarrow[RuO_4^{-2}\,(\text{fast})]{Fe(CN)_6^{-3},\ OH^-} \text{Final product} \quad \text{(v)}$$

where s stands for substrate.

The first step of the proposed mechanism involves the addition of hydroxyl ion to ruthenate ion, second step involves the formation of complex between ruthenate ion and substrate. The complex thus formed in the second step undergoes slow disproportionation giving reduced form of ruthenium in the form of hydrated ruthenium dioxide and corresponding intermediate product. The intermediate product is oxidised quickly to give final product in the last step. The production of hydrated ruthenium dioxide in step(iii) and regeneration of RuO_4^{-2} has been proved by separate experiments. A few experiments have been performed without addition of hexacyanoferrate(III) and thus produced black precipitate has been washed by water many times in gooch crucible and mixed with little alkali and hexacyanoferrate(III), resulted solution is capable of acting as catalyst and this solution exhibit the spectrum which is identical with the spectrum of ruthenate ion (fig. 2.1). Hence steps (III) and (iv) in the proposed mechanism are justified.

On the basis of experimental results and the steps (i) to (v) involved in the proposed mechanism the following rate expression can be derived. The rate of oxidation in terms of decreasing concentration of hexacyanoferrate(III) can be written as:

$$\frac{-d[Fe(CN)_6]^{-3}}{dt} = k\,[(Complex)^{-2}] \qquad (4.8)$$

From step (ii) the concentration of complex is given as

$$[(Complex)^{-2}] = K_1\,[S]\,[RuO_4^{-2}] \qquad (4.9)$$

Now in the first step some of the ruthenate ion or ruthenium(VI) is presented in the form of $(RuO_4.OH)^{-3}$ and some of ruthenium(VI) is present in the form of complex (C). Therefore the total concentration of ruthenium(VI) at particular instant would be given as:

$$[RuO_4^{-2}]_T = [(RuO_4.OH)^{-3}] + [(Complex)^{-2}] + [RuO_4^{-2}] \qquad (4.10)$$

Where T stands for total. On substituting the value of $[(Complex)^{-2}]$ from equation (4.9) and the value of $[RuO_4.OH)^{-3}]$ from the equation (i) in equation (4.10), the following equation is obtained.

$$[RuO_4^{-2}]_T = K[RuO_4^{-2}][OH^-] + K_1[RuO_4^{-2}][S] + [RuO_4^{-2}] \qquad (4.11)$$

Thus the $[RuO_4^{-2}]$ can be written as –

$$[RuO_4^{-2}] = \frac{[RuO_4^{-2}]_T}{1 + K_1[S] + K[OH^-]} \qquad (4.12)$$

Now the rate expression in terms of total concentration of ruthenate ion, considering the equation (4.8), (4.9) and (4.12) can be written as–

$$\frac{-d[Fe(CH)_6^{-3}]}{dt} = \frac{kK_1[S][RuO_4^{-2}]_T}{1 + K_1[S] + K[OH^-]} \qquad (4.13)$$

The rate law is consistent with the observed results, should be given in terms of actual decrease in the concentration of hexacyanoferrate(III) and

equation (4.13) can be written as–

$$\frac{-d[Fe(CH)_6]^{-3}}{dt} = \frac{n\,k K_1 [S]\,[RuO_4^{-2}]_T}{1 + K_1[S] + K[OH^-]} \qquad (4.14)$$

The factor (n) in equ. (4.14) is introduced because stoichiometric studies show that (n) molecules of hexacyanoferrated(III) are being consumed by one molecule of substrate.

The rate expression (4.14) clearly explains the observed experimental results i.e. velocity is directly proportional to ruthenate ion. (Fig. 3.6 to 3.10), zero order in hexacyanoferrate(III) (Fig. 3.1 to 3.5). The velocity is linearly proportional with [S] (Fig. 3.16 to 3.20) in its lower range of concentration but at higher concentration of substrate, the deviation occurs i.e. Michaelis. Menten type of behaviour is observed and rate decreases as the concentration of hydroxide ion increases.

The rate expression (4.13) can be rearranged as:

$$\frac{1}{\text{Rate}} = \frac{1}{n\,k K_1 [S][RuO_4^{-2}]_T} + \frac{1}{n\,k\,[RuO_4^{-2}]_T} + \frac{K[OH^-]}{n\,k K_1 [S][RuO_4^{-2}]_T} \qquad (4.15)$$

According to above equation plots Rate^{-1} Vs. $[S]^{-1}$ and Rate^{-1} Vs. $[OH^-]$ should yield straight line with a positive intercept on y axis.

1. The plots $(-dc/dt)^{-1}$ Vs. $[S^{-1}]$ (fig. 5.1, 5.3, 5.5, 5.7, 5.9) were made and a straight line with a positive intercept on y axis were obtained hence supports the validity of the rate expression (4.15).

2. The plots $(-dc/dt)^{-1}$ Vs. $[OH^-]$ have been made (fig. 5.2, 5.4, 5.6, 5.8, 5.10). The plots are linear with an intercept on y axis supporting

thereby the rate equation (4.15) and hence the proposed mechanism.

3. The plots $(-dc/dt)^{-1}$ Vs. [Ru(VI)] are linear (fig. 3.6 to 3.10) hence supports the validity of derived rate expression (4.13).

With the help of intercept $\left(1/nk\,[RuO_4^{-2}]_T\right)$ of plots $Rate^{-1}$ Vs. $[S]^{-1}$ (fig. 5.1, 5.3, 5.5, 5.7, 5.9) numerical value of k has been calculated in each case. By knowing the value of k and with the help of slopes of plots $Rate^{-1}$ Vs. $[OH^-]$ (Fig. 5.2, 5.4, 5.6, 5.8, 5.10) and Rate Vs. [Ru(VI)] (fig. 3.6 to 3.10) the values of K and K_1 have been calculated for each compound and given in the subsequent pages.

In support of the proposed mechanism the value of K_1 is again calculated with the help of intercept $\left(\frac{1}{nkK_1[RuO_4^{-2}]_T[S]}+\frac{1}{nk[RuO_4^{-2}]_T}\right)$ of plot $Rate^{-1}$ Vs. $[OH^-]$.

By knowing the numerical value of k, K and K_1 and substituting the values in the rate equation (4.14) for all studied compounds, the rate of reaction can also be calculated. The observed (k_s) and calculated (k_s) values of the rate of the reaction (tables 5.1 to 5.5) agree with in 4±4% which again supports the validity of the expression (4.14) and hence proposed mechanism.

5.4 MECHANISM OF OXIDATION OF 4-METHYL PENTANOL-2

In order to explain the observed kinetic data the tentative mechanistic path for ruthenium(VI) catalysed oxidation of 4-methyl pentanol-2 can be written as follows:

$$RuO_4^{-2} + OH^- \underset{}{\overset{K}{\rightleftharpoons}} (RuO_4.OH)^{-3} \quad \text{(i)}$$

$$RuO_4^{-2} + CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2CHOHCH_3 \xrightarrow{K_1} (RuO_4.CH_3CHOHCH_2\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_3)^{-2} \quad \text{(ii)}$$

Complex

$$\left(RuO_4.CH_3CHOHCH_2\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_3\right)^{-2} \xrightarrow[+H_2O]{k} RuO_2.x\,H_2O +$$

$$\left[CH_3-\underset{\displaystyle CH_3\ CH_3}{\underset{|}{CH}}-CH_2\rangle CHO\right] \text{ Intermediate product} + 2OH^- \quad \text{(iii)}$$

$$RuO_2\ x\,H_2O + 4OH^- + 2Fe(CN)_6^{-3} \xrightarrow{\text{fast}} RuO_4^{-2} + 2Fe(CN)_6^{-4} + (x+2)H_2O \quad \text{(iv)}$$

$$\underset{\text{Intermediate product}}{\left[CH_3-\underset{\displaystyle CH_3\ CH_3}{\underset{|}{CH}}-CH_2\rangle CHO\right]} \xrightarrow[RuO_4^{-2}\ (\text{fast})]{Fe(CN)_6^{-3},\ OH^-} \underset{\text{4-methyl pentanone-2}}{CH_3-\underset{\displaystyle CH_3\ H_3C}{\underset{|}{CH}}-CH_3\rangle CO} \quad \text{(v)}$$

Thus corresponding ketone was produced through catalysed route oxidation of 4-Me-pentanol-2. In the above tentative scheme the actual mole of hexacyanoferrate (III) consumed permole of 4-Me-pentanol-2 is two.

Hence rate expression in terms of actual moles of decreasing concentration of hexacyanoferrate(III) might be written as:

$$\frac{-d[Fey]}{dt} = \frac{2k\,K_1[\text{4-Methyl pentanol-2}][Ru(VI)]_T}{1+K_1[\text{4-Methyl pentanol-2}]+K[OH^-]} \quad (4.16)$$

The above equation can be rearranged in the form of

$$\frac{1}{\text{Rate}} = \frac{1+K[OH^-]}{2k\,K_1[RuO_4^{-2}]} \cdot \frac{1}{[\text{4-Methyl pentanol-2}]} + \frac{1}{2k[RuO_4^{-2}]_T} \quad (4.17)$$

The validity of the above equation (4.17) can be tested on the basis of observed experimental results, as follows:

1. The plot, inverse of the reaction velocity i.e. $(Rate)^{-1}$ Vs. [4-methyl pentanol-2] was made (fig. 5.1) a straight line with a positive intercept on y-axis ($Rate^{-1}$) axis is obtained supports the tentative mechanism. From the intercept the value of k i.e. disproportionation constant of the complex may be calculated and it comes out to be 32.76 min^{-1} at 35°C for the following set of reaction.

$$[Fe(CN)_6^{-3}] = 2.0\times10^{-3}m;\ [OH^-] = 1.0\times10^{-1}M;\ [Ru(VI)] = 2.18\times10^{-6}M$$

2. Further the plots between the reaction velocity i.e. (Rate) against $[RuO_4^{-2}]$ were made (fig. 3.6) and a straight line with a unit slope has been obtained. The slope of this straight line will be equal to.

$$\frac{2\,k\,K_1[4-\text{methyl pen tan ol}-2]}{1+K_1[4-\text{methyl pen tan ol}-2]+K[OH^-]}$$

By knowing the value of slope and k the value of K_1 is obtained i.e. 53.26.

3. The plot between inverse of reaction velocity i.e. $(Rate)^{-1}$ and $[OH^-]$ was made (fig. 5.2) and a straight line with a positive intercept on y-axis is obtained.

The value of slope of this plot is equal to $(K/2\ k\,K_1[4-\text{methyl pen tan ol}-2]$ $[RuO_4^{-2}]_T)$. With the help of the value of slope and substituting the value of k, [4-methyl pentanol-2] and $[RuO_4^{-2}]$ the value of K_1 comes out to be 58.37.

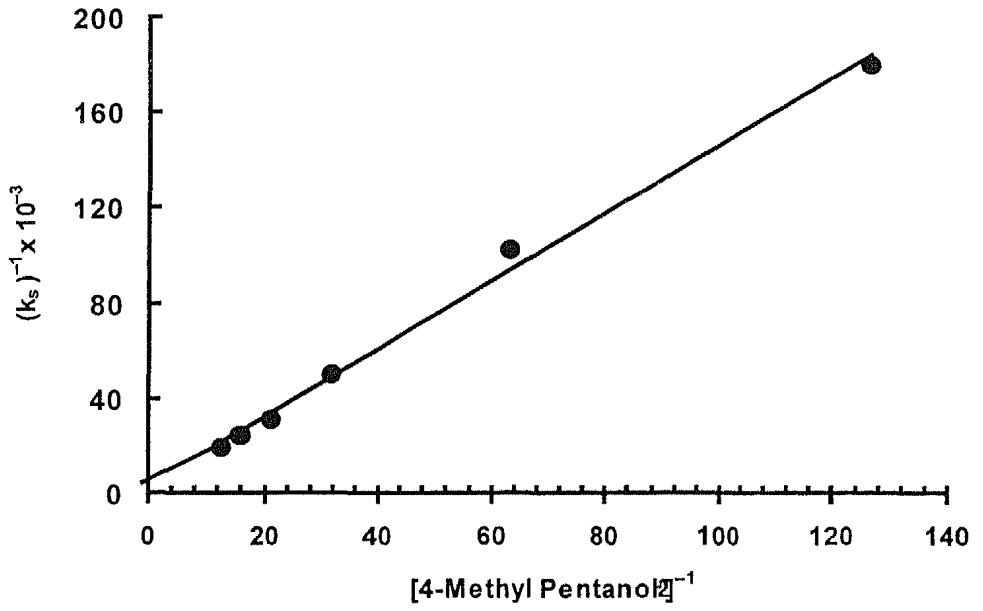


Figure 5.1

Temp.= 35°C; $[K_3Fe(CN)_6] = 2.00 \times 10^{-3}$ mol dm^{-3}; $[OH^-]$=10.00 × 10^{-2} mol dm^{-3} [Ru(VI)]= 2.18×10^{-6} mol dm^{-3}; μ = 0.25 mol dm^{-3};

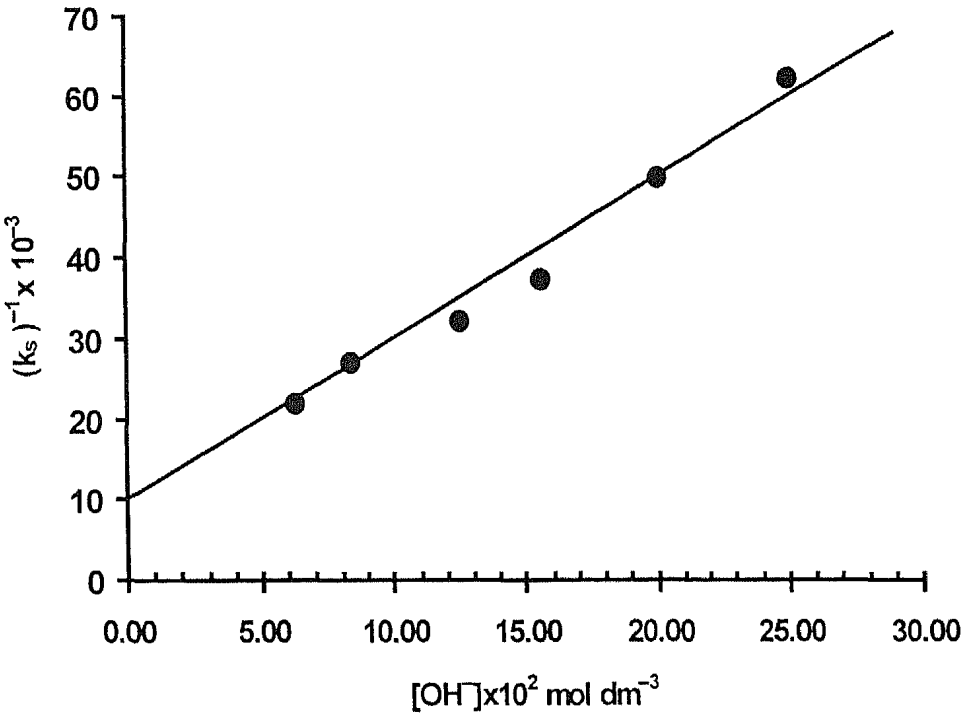


Figure 5.2

Temp.= 35°C; $[K_3Fe(CN)_6] = 2.00 \times 10^{-3}$ mol dm^{-3}; [4-Methyl Pentanol-2]=4.00×10^{-2} mol dm^{-3} [Ru(VI)]= 2.18×10^{-6} mol dm^{-3}; μ = 0.25 mol dm^{-3};

The values of K_1 obtained by two different methods are very close to each other, which supports the validity of the rate expression (4.17) and hence the proposed mechanism.

The validity of rate law is further verified by comparing the observed and calculated values of the reaction rates. For substrate variation, (Table 3.127) catalyst variation (Table 3.47) and OH^- ion variation (Table 3.87) the values of k_s have been calculated and given in the table (5.1).

It is now evident from table (5.1) that the values of k_s observed and k_s calculated are in close agreement which again supports the validity of the equation (4.16).

Table 5.1

Temp. = 35°C

$[K_3Fe(CN)_6]$ = 2.00×10^{-3} mole dm^{-3}

μ = 0.25 mole dm^{-3}

[4-methyl pentanol-2]$\times 10^2$ mole dm^{-3}	$[OH^-]\times10^2$ mole dm^{-3}	$[Ru(VI)]\times10^6$ mole dm^{-3}	$k_s \times 10^6$ mole dm^{-3} min^{-1} observed	$k_s \times 10^6$ mole dm^{-3} min^{-1} calculated
7.90	10.00	2.18	51.80	50.60
6.32	10.00	2.18	40.60	43.61
4.74	10.00	2.18	31.50	35.42
3.16	10.00	2.18	20.00	25.72
1.58	10.00	2.18	9.75	14.14
0.79	10.00	2.18	5.52	7.43
4.00	10.00	6.54	97.50	93.24
4.00	10.00	5.45	78.25	77.70
4.00	10.00	4.36	63.00	62.16
4.00	10.00	3.27	45.75	46.62
4.00	10.00	2.61	38.40	37.21
4.00	10.00	2.18	31.40	31.08
4.00	25.00	2.18	16.00	15.38
4.00	20.00	2.18	20.25	18.49
4.00	15.60	2.18	26.40	22.50
4.00	12.50	2.18	30.95	26.57
4.00	8.30	2.18	36.77	35.14
4.00	6.25	2.18	44.67	41.74

Mean deviation from observed reaction rate = ±2.24%

5.5 MECHANISM OF OXIDATION OF 2-METHOXY ETHANOL:

The steps involved in the oxidation of 2-methoxy ethanol can be represented by the following scheme:

$$RuO_4^{-2} + OH^- \overset{K}{\rightleftharpoons} (RuO_4.OH)^{-3} \quad (1)$$

$$RuO_4^{-2} + CH_3O-CH_2-CH_2OH \overset{K_1}{\rightleftharpoons} (CH_3O-CH_2-CH_2OH.RuO_4)^{-2} \quad (2)$$

Complex

$$(CH_3O-CH_2-CH_2OH.RuO_4)^{-2} \xrightarrow[X\ H_2O]{k} RuO_2.xH_2O + 2OH^-$$

$$+ CH_3O.CH_2.CHO \text{ Intermediate product.} \quad (3)$$

Methoxy acetaldehyde

$$RuO_2.xH_2O + 2Fe(CN)_6^{-3} + 4OH^- \xrightarrow{fast} RuO_2 + 2Fe(CN)_6^{-4} + (x+2)H_2O \quad (4)$$

$$CH_3O.CH_2.CHO \xrightarrow[RuO_4^{-2}\ fast]{Fe(CN)_6^{-3},\ OH^-} CH_3O.CH_2.COOH \quad (5)$$

Intermediate product Final product

Considering the equivalence the final equation i.e., rate law can be written as:

$$\frac{-d\,Fey}{dt} = \frac{4\,k\,K_1\,[2\text{-Methoxy ethanol}][Ru(VI)]_T}{1+K_1\,[2\text{-Methoxy ethanol}]+K[OH^-]} \quad (6)$$

The above rate law can be written as:

$$\frac{1}{Rate} = \frac{1}{4kK_1[2-methoxyethanol][RuO_4^{-2}]_1} + \frac{1}{4K[RuO_4^{-2}]_T}$$

$$+ \frac{K[OH^-]}{4kK_1[2\text{-Methoxy ethanol}]\ [RuO_4^{-2}]} \quad (7)$$

1. According to equation (7), a plot of $(Rate)^{-1}$ Vs. $[2\text{-methoxy-ethanol}]^{-1}$ should yield a straight line with a positive intercept on Y-axis as:

$$\frac{1}{4k[RuO_4^{-2}]_T}$$

The value of intercept is obtained as 2.5×10^3 (fig. 3.29) at 35°C. With the help of this value k has been calculated as 64.51 min^{-1}.

2. Similarly, a plot of $(Rate)^{-1}$ Vs. $[OH^-]$ yields a straight line with an intercept as:

$$\frac{1}{4kK_1[2-methoxy-ethanol][RuO_4^{-2}]_T}+\frac{1}{4k[RuO_4^{-2}]_T} \quad (4.18)$$

On substituting the value of k_1 [2-methoxy-ethanol] and $[RuO_4^{-2}]_T$, the value of K_1 comes out to be 25.02. And the slope of this straight line comes out to be equal to :

$$\frac{K}{4kK_1[2-methoxy-ethanol][RuO_4^{-2}]_T}$$

3. It is evident from the equation (6) that a straight line is again obtained when a plot is made between rate of reaction Vs. $[RuO_4^{-2}]$ and

$$Slope = \frac{4kK_1[2-methoxy-ethanol]}{1+K_1[2-methoxy-ethanol]+K[OH^-]} \quad (I)$$

On substituting the value of k in I, equation, the value of K_1 is obtained as 23.68. Thus the value of K_1 obtained in section (2) is more or less equal to the value obtained in section (3) which support the proposed mechanism. The value of K is obtained 22.31.

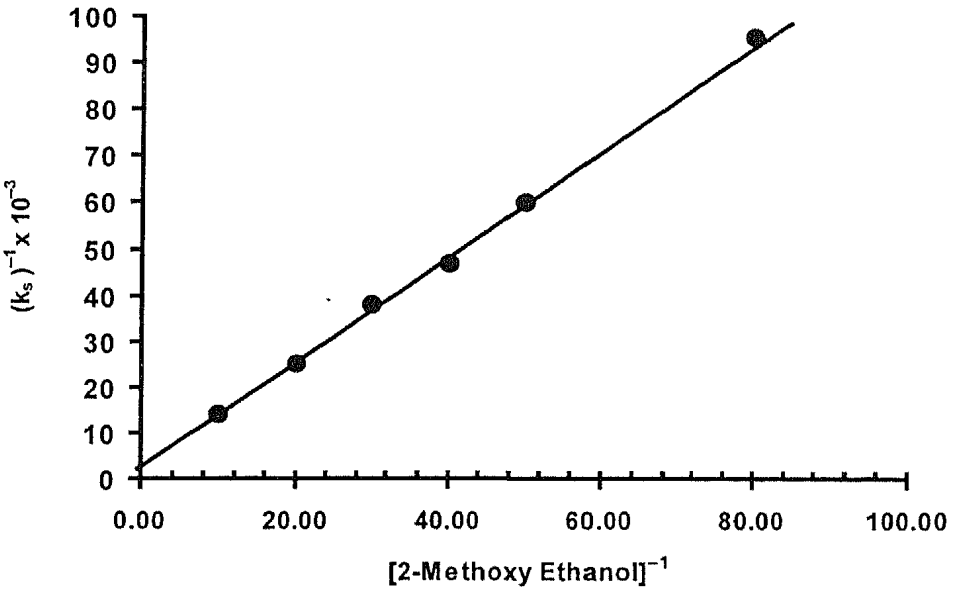


Figure 5.3

Temp.= 35°C; $[K_3Fe(CN)_6] = 2.00 \times 10^{-3}$ mol dm^{-3}; $[OH^-] = 10.00 \times 10^{-2}$ mol dm^{-3} [Ru(VI)]= 15.5×10^{-7} mol dm^{-3}; $\mu = 0.20$ mol dm^{-3};

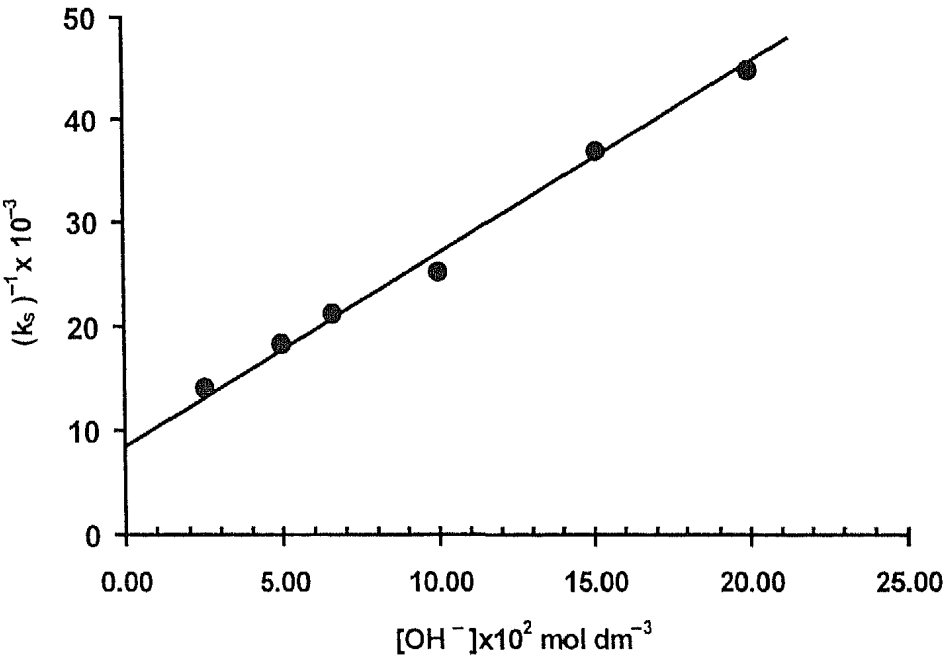


Figure 5.4

Temp.= 35°C; $[K_3Fe(CN)_6] = 2.00 \times 10^{-3}$ mol dm^{-3}; [2-Methoxy Ethanol]=5.00×10^{-2} mol dm^{-3} [Ru(VI)]= 15.5×10^{-7} mol dm^{-3}; $\mu = 0.20$ mol dm^{-3};

The validity of the rate law was further verified by comparing the observed and calculated values of reaction rate from the equation. Some reaction was examined under different experimental conditions at 35°C and corresponding values of reaction rate were also calculated from equation. The experimentally observed and calculated values are given in table (5.2).

A perusal of the table (5.2) clearly indicates that the values obtained by calculation are very much close to the observed values. Thus the above rate law (III) is valid and hence the proposed steps for the oxidation of 2-methoxy-ethanol are justified.

Table 5.2

Temp. = 35°C

$[K_3Fe(CN)_6]$ = 2.00×10^{-3} mole dm^{-3}

μ = 0.20 mole dm^{-3}

[2-methoxy ethanol]$\times 10^2$ mole dm^{-3}	$[OH^-]\times10^2$ mole dm^{-3}	$[Ru(VI)]\times10^7$ mole dm^{-3}	$k_s \times 10^6$ mole dm^{-3} min^{-1} observed	$k_s \times 10^6$ mole dm^{-3} min^{-1} calculated
10.00	10.00	15.50	70.00	75.02
5.00	10.00	15.50	39.60	41.48
3.33	10.00	15.50	26.20	28.62
2.50	10.00	15.50	21.40	21.87
2.00	10.00	15.50	16.60	17.69
1.25	10.00	15.50	10.40	11.24
2.50	10.00	7.50	10.40	10.94
2.50	10.00	15.50	21.40	21.88
2.50	10.00	23.25	32.90	32.82
2.50	10.00	31.00	42.20	43.76
2.50	10.00	38.75	53.00	54.70
2.50	10.00	46.50	63.60	65.64
5.00	20.00	15.50	22.20	22.93
5.00	15.10	15.50	27.00	29.37
5.00	10.00	15.50	39.60	41.48
2.50	20.00	15.50	13.40	11.80
2.50	15.10	15.50	16.20	15.24
2.50	10.00	15.50	21.40	21.87

Mean deviation from observed reaction rate = ±1.45%

5.6 MECHANISM OF OXIDATION OF DIETHYLENE GLYCOL:

In order to explain the observed kinetic data the tentative mechanistic path for ruthenium (VI) catalysed oxidation of diethylene glycol can be written as follows:

$$RuO_4^{-2} + OH^- \overset{K}{\rightleftharpoons} (RuO_4.OH)^{-3} \quad (I)$$

$$RuO_4^{-2} + O(CH_2.CH_2.OH)_2 \overset{K_1}{\rightleftharpoons} \left[O(CH_2.\underset{|}{CH}(OH).CH_2.RuO_4)(CH_2.CH_2.OH)\right]^{-2} \quad (II)$$

(Diethylene glycol) (Complex)

$$\left[O(CH_2.\underset{|}{CH}(OH).CH_2.RuO_4)(CH_2.CH_2.OH)\right]^{-2} \xrightarrow[x H_2O]{k} RuO_2.xH_2O + O(CH_2.CHO)(CH_2.CH_2.OH) + 2OH^- \quad (III)$$

(Complex) (Diglycoladehyde)

$$O(CH_2.CHO)(CH_2.CH_2.OH) + 2OH^- \xrightarrow[OH^-, Fe(CN)_6^{-3}]{RuO_4^{-2}} O(CH_2.COOH)(CH_2.COOH) \quad (IV$$

(Diglycoladehyde) (Diglycolic acid)

$$RuO_2.xH_2O + 2Fe(CN)_6^{-3} + 4OH^- \xrightarrow{fast} RuO_4^{-2} + 2Fe(CN)_6^{-4} + (x+2)H_2O \quad (V)$$

The complex formed in the second step between ruthenate ion and a molecule of diethylene glycol disproportionates into ruthenium(VI) hydroxide species via hydride ion abstraction from the α-carbon atom of diethylene glycol molecule in III step. Intermediate product immediately

reacts with a molecule of hydroxide ion, gives a molecule of diglycolic acid (step-IV). The formation of diglycolic acid was confirmed by the method already given in second chapter. In the last step hexacyanoferrate(III) reacts immediately in the presence of hydroxide ion, with xH_2O species and regenerate catalyst.

Considering the actual moles of hexacyanoferrate(III) used, the final rate law might be written as follows:

$$\frac{-d\,Fey}{dt} = \frac{2k\,K_1[\text{Diethylene glycol}][RuO_4^{-2}]_T}{1+K_1[\text{Diethylene glycol}]+K[OH^-]} \qquad (4.19)$$

The above equation can be written in the form of equation (4.20):

$$\frac{1}{\text{Rate}} = \frac{1}{2kK_1[\text{Diethylene glycol}][RuO_4^{-2}]} + \frac{1}{2k[RuO_4^{-2}]_T} + \frac{K\,OH^-}{2kK_1[\text{Diethylene glycol}][RuO_4^{-2}]_T} \qquad (4.20)$$

$$\text{i.e.;} \quad \frac{1}{\text{Rate}} = \frac{1+K[OH^-]}{2kK_1[RuO_4^{-2}]_T} + \frac{1}{[\text{Diethylene glycol}]} + \frac{1}{2k[RuO_4^{-2}]_T}$$

The validity of the above equation (4.20) can be explained, on the basis of experimental results, as follows:

1. The plots, inverse of the reaction velocity i.e. $(\text{Rate})^{-1}$ against $[\text{Diethylene glycol}]^{-1}$ were made (fig. 5.5) and a straight line is obtained which gives a positive intercept on Y-axis supporting the tentative mechanism of reaction. From the intercept the value of k may be calculated and it comes out to be 45.53 min^{-1} at 35°C for the following set of reaction:

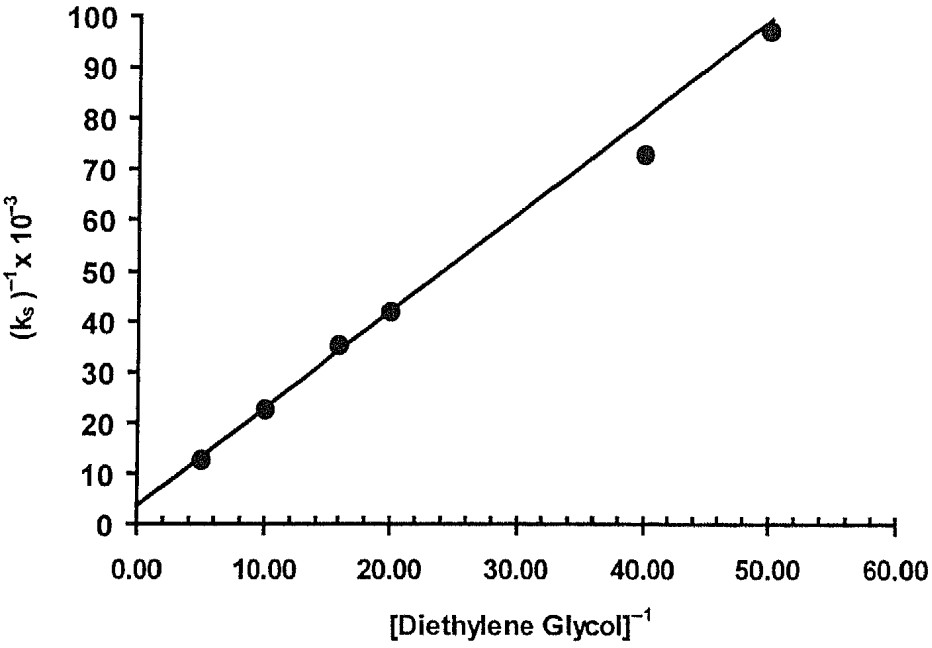


Figure 5.5

Temp.= 30°C; $[K_3Fe(CN)_6] = 2.00 \times 10^{-3}$ mol dm^{-3}; $[OH^-] = 2.00 \times 10^{-1}$ mol dm^{-3} [Ru(VI)]= 3.66×10^{-6} mol dm^{-3}; $\mu = 0.25$ mol dm^{-3};

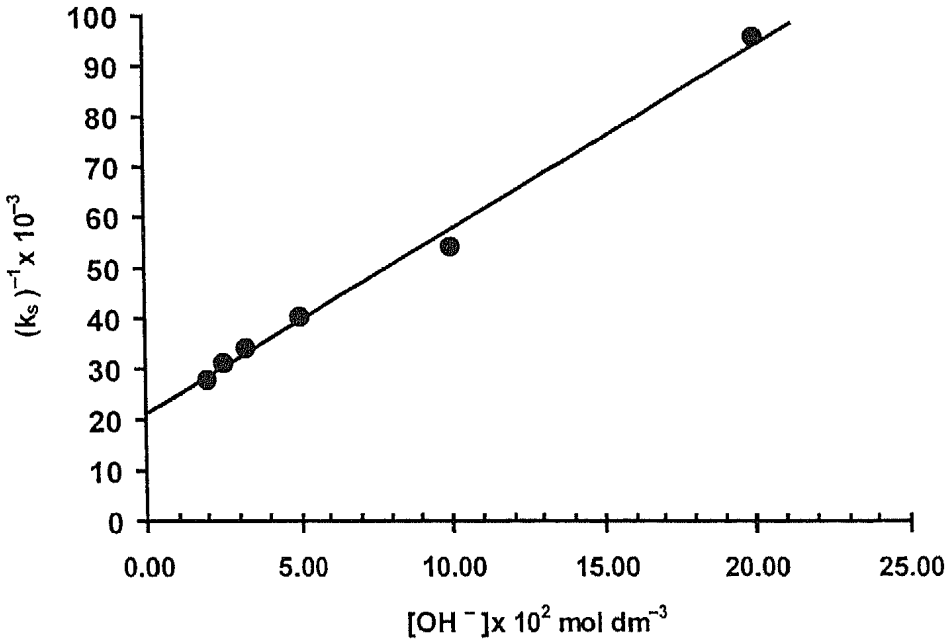


Figure 5.6

Temp.= 30°C; $[K_3Fe(CN)_6] = 2.00 \times 10^{-3}$ mol dm^{-3}; [Diethylene Glycol] $= 2.00 \times 10^{-2}$ mol dm^{-3} [Ru(VI)]= 3.66×10^{-6} mol dm^{-3}; $\mu = 0.25$ mol dm^{-3};

$[Fe(CN)_6^{-3}] = 2.0\times10^{-3}$; $[OH^-] = 2.0\times10^{-1}$M; $[Ru(VI)] = 3.66\times10^{-6}$M.

The slope of this straight line is $1+K[OH^-]/2kK_1[RuO_4^{-2}]_T$. Here an assumption can be made that $1>>K[OH^-]$ due to the fact that the value of K is small as it has been discussed previously. Therefore, the slope can be taken equal to $\frac{1}{2}kK_1[RuO_4^{-2}]_T$ and from this, the value of K_1 comes out to be 7.9, which shows that formation constant of complex is very small.

2. Further the plots between the reaction velocity i.e. (Rate) and $[RuO_4^{-2}]$ were made (Fig. 3.8A) and a straight line has been obtained. The slope of this straight line comes out to be equal to $2kK_1[S]/1+K_1[S]+K[OH^-]$, where 'S' stands for diethylene glycol. Here, again, the inequality $(1+K_1[S])>>K[OH^-]$ holds good based on the fact that the value of K is 19.6. The value of K_1 comes out to be 6.18 which is quite close with the value obtained supporting the proposed reaction mechanism.

Table 5.3

Temp. = 30°C

$[K_3Fe(CN)_6]$ = 2.00×10^{-3} mole dm^{-3}

μ = 0.20 mole dm^{-3}

[Diethylene glycol]$\times 10^2$ mole dm^{-3}	$[OH^-]\times10^2$ mole dm^{-3}	$[Ru(VI)]\times10^6$ mole dm^{-3}	$k_s \times 10^6$ mole dm^{-3} min^{-1} observed	$k_s \times 10^6$ mole dm^{-3} min^{-1} calculated
20.00	20.00	3.66	78.60	81.01
10.00	20.00	3.66	44.60	46.11
6.25	20.00	3.66	28.38	30.41
5.00	20.00	3.66	24.00	24.76
2.50	20.00	3.66	13.70	12.86
2.00	20.00	3.66	10.24	10.36
2.00	10.00	1.82	6.50	6.68
2.00	10.00	3.66	14.00	16.88
2.00	10.00	5.47	19.06	20.03
2.00	10.00	7.33	25.25	26.76
2.00	10.00	9.12	32.34	33.43
2.00	10.00	10.95	38.65	40.11
2.00	20.00	3.66	10.38	10.36
2.00	10.00	3.66	18.48	16.88
2.00	5.00	3.66	24.72	24.62
2.00	3.25	3.66	29.52	29.33
2.00	2.50	3.66	32.16	31.95
2.00	2.00	3.66	36.00	33.97

Mean deviation from observed reaction rate = ±1.10%

5.7 MECHANISM OF OXIDATION OF TRIETHYLENE GLYCOL:

On this basis of experimental data the following reaction mechanism may be proposed for the oxidation of triethylene glycol with hexacyanoferrate(III) using Ru(VI) as a homogeneous catalyst.

$$RuO_4^{-2} + OH^- \overset{K}{\rightleftharpoons} (RuO_4.OH)^{-3} \qquad (I)$$

$$RuO_4^{-2} + HO-CH_2-CH_2-O-CH_2-CH_2-O-CH_2-CH_2-OH \overset{K_1}{\rightleftharpoons}$$

$$(HO-CH_2-CH_2-O-CH_2-CH_2-O-CH_2-CH_2-OH.RuO_4)^{-2} \qquad (II)$$

(Complex)

$$CH_2.CH_2.O.CH_2.CH_2.O.CH_2.CH_2.OH.RuO_4)^{2-} \xrightarrow[x\,H_2O]{k} RuO_2.xH_2O + 2OH^-$$

(Complex)

$$+ HO.CH_2.CH_2.O.CH_2.CH_2.O.CH_2.CHO \qquad (III)$$

(Intermediate product)

$$HO.CH_2.CH_2.O.CH_2.CH_2.O.CH_2CHO \xrightarrow[Fe(CN)_6^{-3}\ OH^-]{RuO_4^{-2}\ fast}$$

$$HOOCCH_2O.CH_2.CH_2.O.CH_2COOH \qquad (IV)$$

(Triglycolic acid)

$$RuO_2.xH_2O + 2Fe(CN)_6^{-3} + 4OH^- \xrightarrow{fast} RuO_4^{-2} + 2Fe(CN)_6^{-4} + (x+2)H_2O \qquad (V)$$

The first step involves the addition of hydroxyl ion to ruthenate ion. The complex formed in the second step between ruthenate ion and a molecule of triethylene glycol undergoes slow disproportionation giving reduced form of ruthenium i.e. ruthenium dioxide and corresponding intermediate product which is further oxidized to give final products. The

oxidation steps may be written as follows:

$$HO-CH_2-CH_2-O-CH_2-CH_2-O-CH_2-CH_2-OH \xrightarrow{[O]} HO-CH_2-$$

$$CH_2-O-CH_2-CH_2-O-CH_2-CHO \xrightarrow{[O]} OHC-CH_2-O-CH_2-CH_2$$

$$O-CH_2-CHO \xrightarrow{[O]} HOOC-CH_2-O-CH_2-CH_2-O-CH_2-COOH$$

Ruthenium dioxide produced in the (III) step is oxidixed by alkaline hexacyanoferrate(III) and ruthenate ion is regenerated in (V) step which is capable of acting as a catalyst.

The final rate equation, considering the actual moles of hexacyanoferrate(III) used by one mole of triethylene glycol can be written as–

$$\frac{-d[Fe(CN)_6^{-3}]}{dt} = \frac{2kK_1[\text{Triethylene glycol}][RuO_4^{-2}]_T}{1+K_1[\text{Triethylene glycol}]+K[OH^-]} \qquad (4.21)$$

The rate expression (4.21) clearly explains the observed experimental results i.e. reaction shows first order dependence on ruthenate on (fig. 3.9). The rate of the reaction increases with increase in substrate concentration and shows Michaelis Menten (fig. 5.7) type of behaviour. The effect of alkali is Marginal and rate decreases with increase in hydroxide ion concentration.

This equation may also be rewritten as–

$$\frac{1}{\text{Rate}} = \frac{1}{2kK_1[\text{Triethylene glycol}][RuO_4^{-2}]} + \frac{1}{2k[RuO_4^{-2}]_T} + \frac{K[OH]^-}{2kK_1[\text{Triethylene glycol}][RuO_4^{-2}]_T} \qquad (4.22)$$

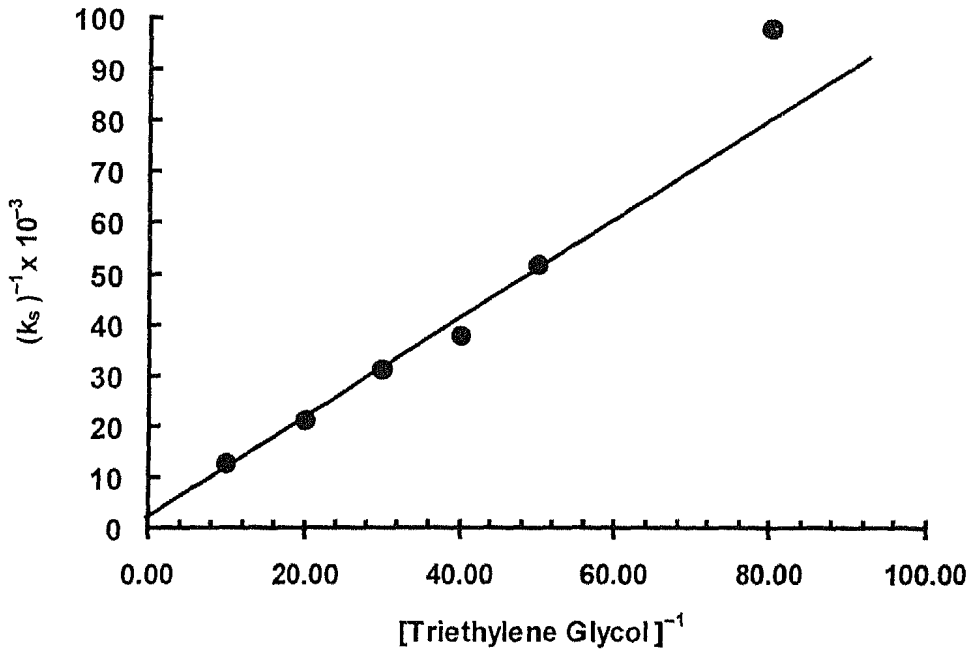


Figure 5.7

Temp.= 35°C; $[K_3Fe(CN)_6] = 2.00 \times 10^{-3}$ mol dm^{-3}; $[OH^-] = 10.00 \times 10^{-2}$ mol dm^{-3} [Ru(VI)]= 4.81×10^{-6} mol dm^{-3}; $\mu = 0.20$ mol dm^{-3};

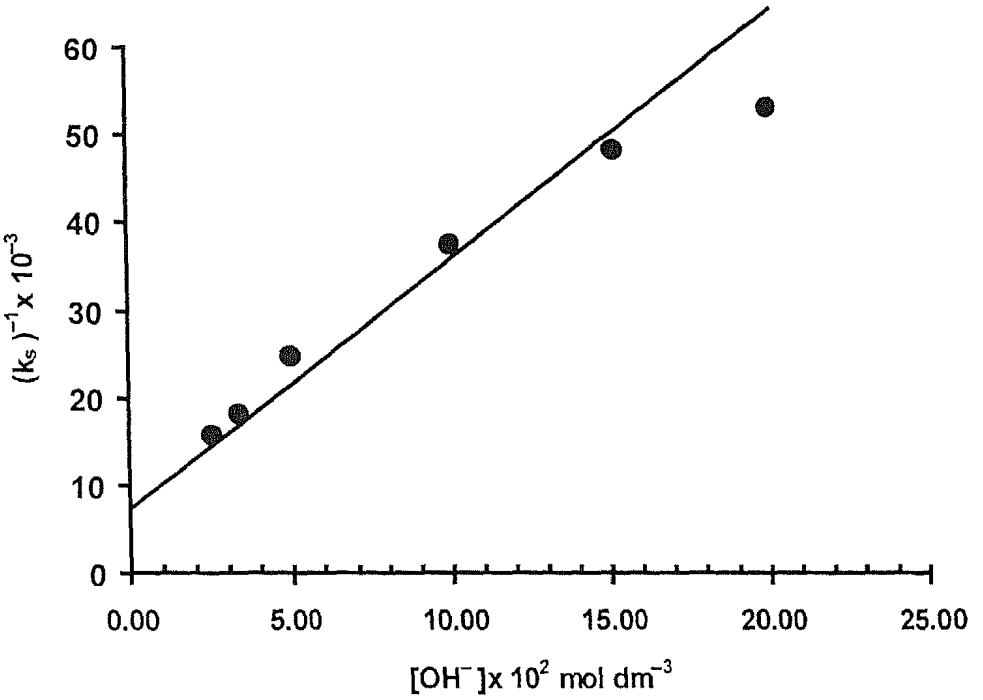


Figure 5.8

Temp.= 35°C; $[K_3Fe(CN)_6] = 2.00 \times 10^{-3}$ mol dm^{-3}; [Triethylene Glycol] $= 2.5 \times 10^{-2}$ mol dm^{-3} [Ru(VI)]= 4.81×10^{-6} mol dm^{-3}; $\mu = 0.20$ mol dm^{-3};

Now an attempt will be made to varify the validity of the rate law (4.22).

1. The plot $(-dc/dt)^{-1}$ Vs. [Triethylene glycol]$^{-1}$ was made (fig. 5.7). This graph clealry shows that straight line is obtained with a positive intercept on Y-axis proving the validity of rate law (3.18) and hence the produced mechanism. From the intercept of this graph which is equal to $\frac{1}{2k[RuO_4^{-2}]_T}$ i.e. $= 2.5\times10^3$ the value of k is calculated which comes out to be 41.6 min^{-1}.

2. Further, the plots between $(-dc/dt)$ and $[RuO_4^{-2}]$ were made (fig. 3.9) and these plots give a straight line passing through the origin, obeying the rate expression (4.21). The slope of this straight line should be equal to $2kK_1[S]/1+K_1[\text{triethylene glycol}]+K[OH^-]$ according to rate law (4.22). By knowing the value of the slope from the graph and substituting the value of k; the value of K_1 is equal to 13.1.

3. The plot between the inverse of reaction velocity i.e. $(-dc/dt)^{-1}$ and $[OH^-]$ was made fig. (5.8), which supports the validity of the rate law (4.22) i.e. a straight line is obtained with a positive intercept on Y-axis. The slope of this straight line is equal to $K/2kK_1$ [triethylene glycol] $[RuO_4^{-2}]$.

Thus the value obtained of K_1 from two methods are very close to each other supports the validity of the rate expression (4.22) and thus the proposed mechanism for triethylene glycol.

The closeness in the values of k_s by experiment and calculation supports the validity of the rate expression (4.21).

Table 5.4

Temp. = 35°C

$[K_3Fe(CN)_6]$ = 2.00×10^{-3} mole dm^{-3}

μ = 0.20 mole dm^{-3}

[Triethylene glycol]$\times 10^2$ mole dm^{-3}	$[OH^-]\times10^2$ mole dm^{-3}	$[Ru(VI)]\times10^6$ mole dm^{-3}	$k_s \times 10^6$ mole dm^{-3} min^{-1} observed	$k_s \times 10^6$ mole dm^{-3} min^{-1} calculated
10.00	10.00	4.81	79.00	78.40
5.00	10.00	4.81	47.20	43.48
3.33	10.00	4.81	32.30	30.05
2.50	10.00	4.81	26.54	23.00
2.00	10.00	4.81	19.36	18.60
1.25	10.00	4.81	10.20	11.84
5.00	10.00	1.20	15.04	10.87
5.00	10.00	2.40	16.06	21.74
5.00	10.00	3.60	35.82	32.61
5.00	10.00	4.81	47.20	43.48
5.00	10.00	6.01	56.00	54.36
5.00	10.00	7.22	68.00	65.23
2.50	20.00	4.81	18.72	13.01
2.50	15.15	4.81	20.60	16.48
2.50	10.00	4.81	26.46	23.00
2.50	5.00	4.81	40.24	37.28
2.50	3.33	4.81	55.40	57.18
2.50	2.50	4.81	63.20	64.10

Mean deviation from observed reaction rate = ±2.85%

5.8 MECHANISM OF OXIDATION OF TETRAETHYLENE GLYCOL:

On the basis of observed kinetic data, a tentative mechanism for Ru(VI) catalysed oxidation of tetraethylene glycol can be written as follows:

$$RuO_4^{-2} + OH^- \overset{K}{\rightleftharpoons} (RuO_4.OH)^{-3} \qquad (I)$$

$$RuO_4^{-2} + HO{-}CH_2{-}CH_2{-}O{-}CH_2{-}CH_2{-}O{-}CH_2{-}CH_2{-}O{-}CH_2{-}CH_2{-}OH \overset{K_1}{\rightleftharpoons}$$

$$\left(O\begin{matrix} CH_2-CH_2-O-CH_2-CH_2-OH-.RuO_4 \\ CH_2-CH_2-O-CH_2-CH_2-OH \end{matrix} \right)^{-2} \qquad (II)$$

(Complex)

$$\left(O\begin{matrix} CH_2-CH_2-O-CH_2-CH_2-CH-.RuO_4 \\ CH_2-CH_2-O-CH_2-CH_2-CH \end{matrix} \right)^{-2} \xrightarrow[xH_2O]{k} RuO_2.xH_2O + \quad (II)$$

$$O\begin{matrix} CH_2-CH_2-O-CH_2-CH_2-OH \\ CH_2-CH_2-O-CH_2-CHO \end{matrix} + 2OH^- \qquad (III)$$

$$O\begin{matrix} CH_2.CH_2.O.CH_2.CH_2.OH \\ CH_2.CH_2.O.CH_2.CHO \end{matrix} \xrightarrow[RuO_4^{-2},\ fast]{Fe(CN)_6^{-3},\ OH^-} O\begin{matrix} CH_2.CH_2.O.CH_2.COOH \\ CH_2.CH_2.O.CH_2.COOH \end{matrix} \qquad (III)$$

$$RuO_2.xH_2O + 2Fe(CN)_6^{-3} + 4OH^- \xrightarrow{fast} RuO_4^{-2} + 2Fe(CN)_6^{-4} + (x+2)H_2O \qquad (V)$$

The first step involves the addition of hydroxyl ion to ruthenate ion. In the second step complex is formed between triethylene glycol molecule and ruthenate ion. The complex thus formed undergoes slow disproportionation giving the reduced form of ruthenium viz., Ru(IV) and

corresponding intermediate product. Ruthenium dioxide produced in step (III) is immediately oxidized to ruthenate ion by hexacyanoferrate(III) and alkali. The catalyst is regenerated in the step (V). Thus step (III) is justified in the proposed mechanism.

Considering the actual moles of hexacyanoferrate(III) consumed in the formation of the product, the final rate expression can be written as:

$$\frac{-d[Fe(CN)_6^{3-}]}{dt} = \frac{2kK_1[\text{tetraethylene glycol}][RuO_4^{2-}]_T}{1+K_1[\text{tetraethylene glycol}]+K[OH^-]} \qquad (4.23)$$

This equation may also be expressed as:

$$\frac{1}{\text{Rate}} = \frac{1+K[OH^-]}{2kK_1[RuO_4^{2-}]_T} \cdot \frac{1}{[\text{tetraethylene glycol}]} + \frac{1}{2k[RuO_4^{2-}]_T} \qquad (4.24)$$

Now an attempt will be made to verify the validity of the rate law in the same way as done in the previous section.

1. The plots were made between $(-dc/dt)^{-1}$ Vs. $[\text{Tetraethylene glycol}]^{-1}$ (fig. 5.9). These graphs clearly show that straight line is obtained with a positive intercept on Y-axis proving the validity of the rate law (4.24) and hence the proposed mechanism. The intercept thus obtained will give the value of k, which is 38.16.

2. Similarly, a plot of $(\text{Rate})^{-1}$ Vs. $[OH^-]$ gives a straight line (fig. 5.10). With an intercept as:

$$\frac{K}{2kK_1[\text{Tetraethylene glycol}][RuO_4^{2-}]_T} + \frac{1}{2k[RuO_4^{2-}]_T} \qquad (4.25)$$

and slope as:

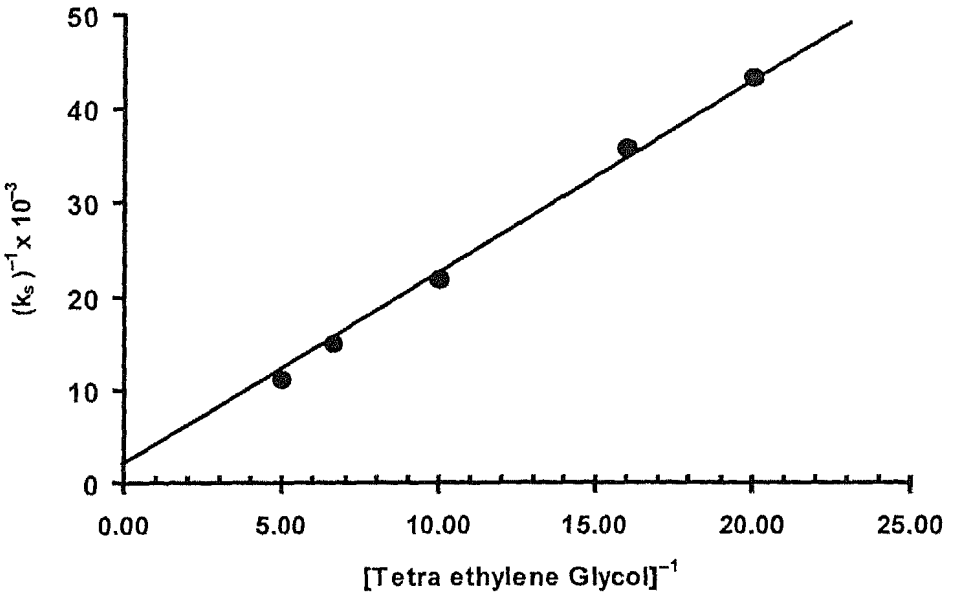


Figure 5.9

Temp.= 35°C; $[K_3Fe(CN)_6] = 2.00 \times 10^{-3}$ mol dm^{-3}; $[OH^-] = 10.0 \times 10^{-2}$ mol dm^{-3} [Ru(VI)]= 6.55×10^{-6} mol dm^{-3}; $\mu = 0.20$ mol dm^{-3};

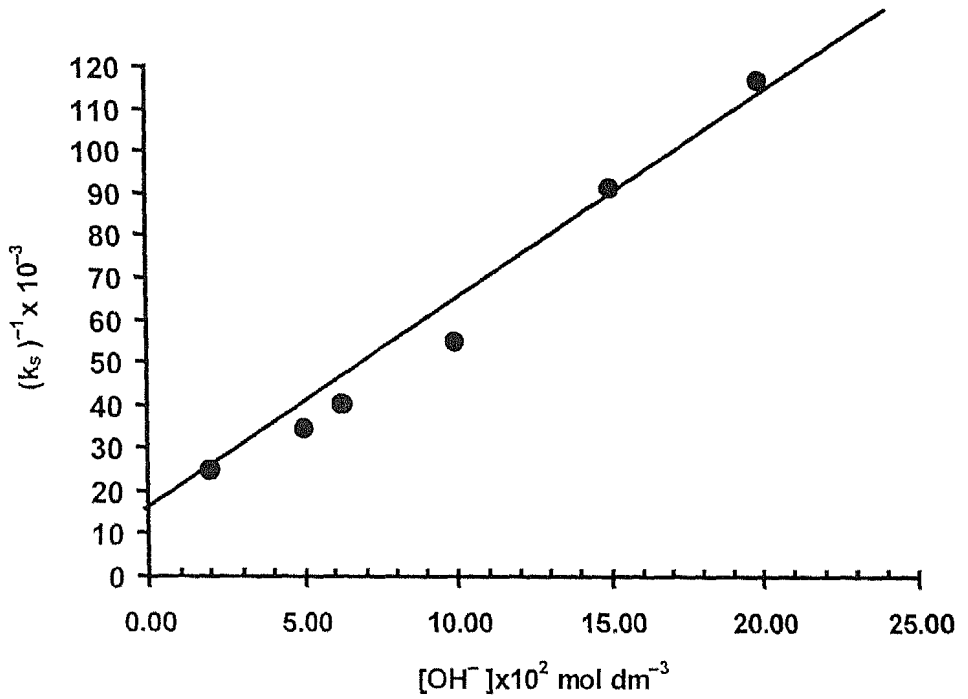


Figure 5.10

Temp.= 35°C; $[K_3Fe(CN)_6] = 2.00 \times 10^{-3}$ mol dm^{-3}; [Tetraethylene Glycol] $= 20.0 \times 10^{-2}$ mol dm^{-3} [Ru(VI)]= 6.55×10^{-6} mol dm^{-3}; $\mu = 0.20$ mol dm^{-3};

$$\frac{K}{2kK_1[\text{Tetraethylene glycol}][RuO_4^{2-}]_T}$$

On substituting the value of k,

Tetraethylene glycol and RuO_4^{2-}, the value of K_1 comes out to be 6.6.

3. It is evident from the equation (4.25) that a straight line is again obtained when a plot is made between rate of the reaction Vs. $[RuO_4^{-2}]$, and the value of slope (Fig. 3.10) is equal to:

$$\frac{2kK_1[\text{Tetraethylene glycol}]}{1+K_1[\text{Tetraethylene glycol}]+K[OH^-]}$$

On substituting the value of k and K, the value of K_1 is calculated as 4.88. Thus the value of K_1 obtained in section (2) is more or less equal to the value obtained in section (3) which supports the proposed mechanism the value of K is obtained as 17.1. Substituting the value of k, K_1 and K in equation (4.23), the rate law can be written as follows in the case of tetraethylene glycol.

$$\frac{-d[Fey]}{dt} = \frac{2\times 38.16\times 4.88\times[\text{Tetraethylene glycol}][RuO_4^{2-}]}{1+4.88[\text{Tetraethylene glycol}]+17.1[OH^-]}$$

The validity of this rate law was further verified by comparing the observed and calculated values of the reaction rate from this equation.

Table 5.5

Temp. = 35°C

$[K_3Fe(CN)_6]$ = 2.00×10^{-3} mole dm^{-3}

μ = 0.20 mole dm^{-3}

[Tetraethylene glycol]$\times 10^2$ mole dm^{-3}	$[OH^-]\times10^2$ mole dm^{-3}	$[Ru(VI)]\times10^6$ mole dm^{-3}	$k_s \times 10^6$ mole dm^{-3} min^{-1} observed	$k_s \times 10^6$ mole dm^{-3} min^{-1} calculated
20.00	20.00	6.55	90.00	86.28
15.00	20.00	6.55	67.00	71.05
10.00	20.00	6.55	46.00	49.70
6.25	20.00	6.55	28.00	32.26
5.00	20.00	6.55	23.00	26.17
2.00	20.00	6.55	8.50	10.80
2.00	10.00	3.27	8.54	8.68
2.00	10.00	6.55	18.20	17.38
2.00	10.00	7.86	21.56	20.85
2.00	10.00	9.82	27.16	26.05
2.00	10.00	11.79	32.86	31.28
2.00	10.00	13.10	37.08	34.76
2.00	20.00	6.55	8.54	10.79
2.00	15.00	6.55	11.02	13.32
2.00	10.00	6.55	18.20	17.37
2.00	6.25	6.55	24.98	22.50
2.00	5.00	6.55	29.06	25.00
2.00	2.00	6.55	40.01	43.89

Mean deviation from observed reaction rate = ±2.42%

5.9 COMPARISON OF RATES OF DISPROPORTIONATION, STABILITY CONSTANT AND FORMATION CONSTANT OF RUTHENATE-DIOL AND ALCOHOL COMPLEXES AND THEIR NET RATES OF OXIDATION:

In this section an attempt has been made to compare the value of formation constant (K_1) and disproportionation constant (k) and the stability constant (K) in case of all studied compounds. All the three constant i.e.; K_1, k and K have been evaluated in proceeding sections and the values are given in following table.

Table 5.6

Stability constants (K) disproportionation constants (k) for diol-ruthenate ion and alcohol-ruthenate ion and formation constant (K_1) of ruthenate ion hydroxide ion.

Substrate	K_1 from OH^- variation	K_1 from RuO_4^{-2} variation	K for ruthenate-hydroxide complex	k min^{-1}
4-methyl pentanol-2	58.37	53.26	19.80	32.76
2-methoxy ethanol	25.02	23.68	20.31	64.51
Diethylene glycol	7.90	6.18	19.60	45.53
Triethylene glycol	16.60	13.10	18.60	41.60
Tetraethylene glycol	6.60	4.88	17.10	38.16

5.10 Thermodynamic parameter for reaction:

In chapter four kinetic studies have been made at different temperatures and thereby energy of activation has been calculated from the slope of the Arrhenius plots fig. (4.1 to 4.5). The entropy of activation ($\Delta S^{\neq}$) and free energy of activation ($\Delta F^{\neq}$) have also been calculated and given in the table (4.7).

More or less identical values of ($\Delta F^{\neq}$) clearly suggests that reaction is taking place through similar route in all the studied compounds. Moreover the linear graph (fig. 5.11) between ΔH and ($\Delta S^{\neq}$) further confirms that the oxidation of all studied compounds take place through similar route.

5.11 GENERAL FEATURES OF THE REACTIONS STUDIES:

In section 3.1, the effect of change in hexacyanoferrate(III) has been studied in detail for three diols and two alcohols. It was observed that in a particular run the value of zero order rate constant remain constant up to 70% of the reaction. But when the concentration of catalyst was kept high the reaction follows zero order kinetics upto more than 85% of the reaction. We could not study all reactions at high catalyst concentration because reactions become too fast to study. The retarding effect can be explained due to deactivation of catalyst.

CONCLUSION:

On the basis of reaction studied the following conclusions are drawn:

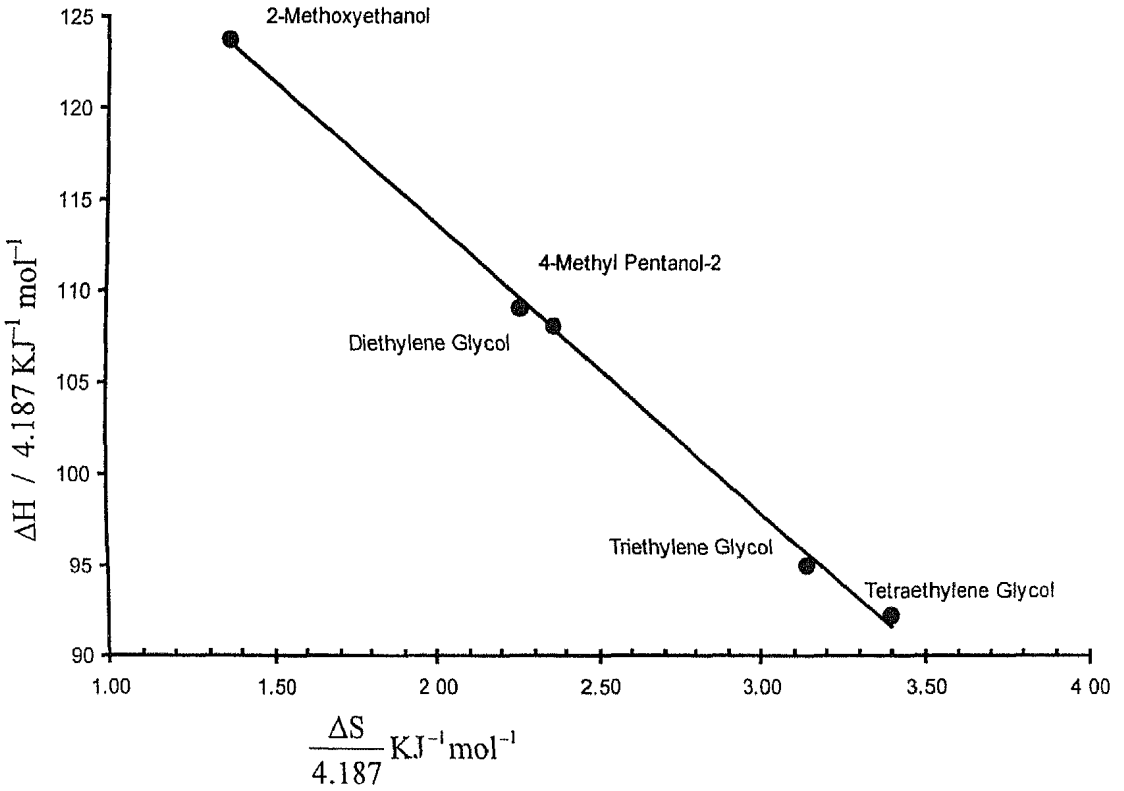

2-Methoxyethanol
4-Methyl Pentanol-2
Diethylene Glycol
Triethylene Glycol
Tetraethylene Glycol
125
120
115
110
105
100
95
90
1.00
1.50
2 00
2.50
3.00
3.50
4 00
ΔH / 4.187 KJ⁻¹ mol⁻¹
ΔS / 4.187 KJ⁻¹mol⁻¹

Figure 5.11

1. This is one of the new system in the literature of kinetics and mechanism of oxidation.

2. This system can safely be employed to convert primary and secondary alcohols to corresponding acids and ketones.

3. With help of this system the idea about the co-ordination of hydroxide with ruthenate ion can be conceived which supports the work of Loma and Brubaker[14].

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